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# Testing the Photocatalytic Oxidation Abilities of Titania-Silica Aerogels Fabricated Using the Rapid Supercritical Extraction Method

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Testing the Photocatalytic Oxidation Abilities of Titania-Silica Aerogels  
Fabricated Using the Rapid Supercritical Extraction Method

By

Lauren B. Brown

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Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Mechanical Engineering

UNION COLLEGE

June 2011

## **ABSTRACT**

BROWN, LAUREN Testing the photocatalytic oxidation abilities of titania-silica aerogels fabricated using the rapid supercritical extraction method.  
Department of Mechanical Engineering, June 2011.

ADVISOR: Ann Anderson

Indoor air has been shown to be four to five times more polluted than outdoor air.

Titania-silica aerogels can photocatalytically oxidize volatile organic compounds found in indoor air. Aerogels are the lightest known solid with 90-99% air by volume. Titania-silica aerogels were fabricated in seven to nine hours using the Rapid Supercritical Extraction method and properties compared well to those published in the literature. Bulk density ranges between 0.025 and 0.04 g/cm<sup>3</sup>. Skeletal density ranges between 1.75 and 2.75g/cm<sup>3</sup>. BET surface area ranges between 200 and 700 m<sup>2</sup>/g. BJH pore distribution showed distinct differences between silica and titania aerogels. FTIR results showed the presence of anatase titania, which has been shown to be a key component in photocatalytic oxidation. Photocatalytic oxidation abilities were tested using methylene blue in an aqueous solution in both natural sunlight and using a solar simulator. Results showed that methylene blue can be decomposed using photocatalytic oxidation in the presence of UV and visible light. A flow-type photocatalytic oxidation test apparatus was designed and built to test the decomposition rate of toluene at various flow rates in the presence of water vapor. Humidified toluene vapor flowed through samples of titania-silica aerogel placed in a reactor vial, illuminated by four 4W UV blacklights surrounding the vial. The effluent stream was analyzed using two different 10.6 eV lamp handheld photoionization detectors. Up to a 99% reduction in toluene concentration was seen. Most

of this reduction is likely due to adsorption of toluene in the aerogel material, although preliminary results show photocatalytic oxidation also does occur.

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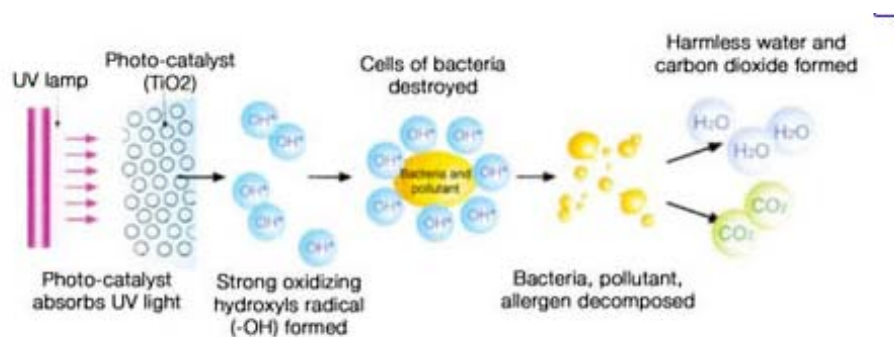
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## **CHAPTER 1: BACKGROUND**

Indoor air has been found to be up to five times more polluted than outdoor air [1]. This becomes increasingly problematic as humans typically spend the majority of their time indoors. One reason for this pollution is the presence of volatile organic compounds, or VOCs. Some of these VOCs are known carcinogens which can pose long term health risks. Furthermore, there is an obvious need to clean the indoor air, ideally in a cheap, green method. The process of photocatalytic oxidation using aerogels is one option to accomplish this goal. This chapter discusses what aerogels are, what photocatalytic oxidation is, and a review of previous research done regarding photocatalytic oxidation with aerogels.

An aerogel is a porous nanostructure with 90-99% air by volume. It has the lowest known density, index of refraction, thermal, electrical and acoustical conductivities of any known solid. Some applications of a typical silica aerogel include comet dust collectors and electrical insulators for NASA, insulation in jackets, boots and suits for divers, insulating windows, chemical absorber for cleaning up spills, and a platform for sensing chemical species. Aerogels can be difficult to make, however the Rapid Supercritical Extraction (RSCE) method developed by the Aerogel Lab at Union College is able to fabricate aerogels much faster than conventional methods (Gauthier et al., 2004). This method has already been used to make silica (Gauthier et al., 2004; Anderson et al., 2009), alumina (Bono et al., 2010), titania and titania-silica aerogels (Brown, et al. 2010). Titania-silica aerogels are of particular interest due to their properties as an adsorbent and photocatalyst. One application using these properties is adsorption and photocatalytic oxidation (PCO) to degrade volatile organic compounds (VOCs).

Photocatalytic oxidation is the process of breaking down chemical molecules using light, resulting in harmless products, namely water and carbon dioxide. It is a technology used in the remediation of organic pollutants since it is economic, simple and easily-implemented. It has shown promise in the removal of VOCs in process airstreams. VOC are defined as a class of indoor air pollutants found in industrial establishments, manufacturing facilities, commercial workplaces, even homes. Most are simply irritants, but some are suspected to be carcinogens that pose significant long-term health risks. The use of centralized air-handling systems in modern buildings where the air is recycled and re-circulated further questions the issue of our exposure to VOCs. PCO has the ability to mineralize simple organic molecules into carbon dioxide and water at ambient conditions using molecular oxygen (Maira et al., 2003).



**Figure 1. Schematic showing photocatalytic oxidation [2].**

### *Literature Review*

Zhao and Yang (2003) compiled a literature review of on the use of photocatalytic oxidation to destruct volatile organic compounds in indoor air. Using PCO has received attention due to its potential application for air purification in nearly any indoor space, including office buildings, factories, homes, cars, and spacecraft. In the presence of air or

oxygen, UV-irradiated titanium dioxide is capable of removing many organic contaminants; however, if the process is incomplete, the intermediates formed during PCO can occupy the active sites of the catalyst and eventually deactivate the catalyst. Deactivation may occur due to generation of reaction residues which cause the loss of active surface sites, or fouling which changes the catalyst surface by blocking pores. The reaction rate of PCO is dependent on the characteristics of the photocatalyst, humidity, reactor type, light source, etc. In terms of photocatalyst,  $\text{TiO}_2$  can be used either on beads, hollow tubes, woven fabric, silica gel, or with methods like the dip coated method and sol-gel method. A reactor should be capable of fairly high gas feed rates, provide efficient contact among UV photons, solid catalyst and gaseous reactants. It was also found that water vapor must be present in order for photocatalytic degradation and total mineralization of  $\text{CO}_2$  to occur. Toluene oxidation rate was found to increase by water concentration up to about 1650 ppmv, with a toluene concentration between 0 and 800 ppmv.

Méndez-Román and Cardona-Martínez (1998) studied the relationship between the formation of surface species and catalyst deactivation during the gas-phase photocatalytic oxidation of toluene. It was noted that the photocatalytic detoxification of volatile organic compounds is typically more efficient in the gas phase than in the liquid phase. In the complete absence of water vapor, the catalyst photooxidation activity rapidly declines with time on stream, however, catalyst activity may be completely or partially recovered by flowing humid air over the catalyst in the presence of UV illumination. In this study, a conventional flow system was used to treat the samples and mass flow controllers were used to establish the flows of the different gases used. Typically, 50mg of catalyst was

pressed into a self-supported 1cm wafer and was activated using flowing oxygen, helium and nitrogen at specified concentrations for a specified amount of time. Toluene concentrations were between 30 and 200ppm and water concentrations of 0 or 1200ppm were used in the study of PCO of toluene. Two catalysts were studied; P-25  $\text{TiO}_2$  and 8%  $\text{SiO}_2$ - $\text{TiO}_2$ , both provided by Degussa, and it was found that the silica-titania catalyst seemed to adsorb a significantly higher amount of toluene than titania at 300K. Additionally, new surface species were formed when adsorbed toluene is irradiated in flowing helium for the  $\text{SiO}_2$ - $\text{TiO}_2$  catalyst, which was not the case for the  $\text{TiO}_2$  catalyst. It was also found that the presence of water slows the formation of surface species, perhaps because the water competes for the sites where the species are formed or it partially regenerates the active sites. It was determined that the presence of water did slow the deactivation of the sample. The  $\text{SiO}_2$ - $\text{TiO}_2$  photocatalyst was more active and appears to deactivate slower than  $\text{TiO}_2$ , specifically in the presence of water vapor, which is encouraging for the current research.

Yoda et al. (2000) discussed the recent interest in the application of inorganic aerogels as catalysts, catalyst supports and adsorbents due to the large specific surface areas, and larger porosities than conventionally dried inorganic gels. The titania aggregates found on the surface of the silica matrix by microscopic observation are expected to function as both adsorbent and photocatalysts. These features could be suitable for the removal of toxic chemicals, such as volatile organic compounds (VOCs) in the atmosphere by both adsorption and decomposition. The adsorption and desorption isotherms of benzene vapor on Yoda's aerogel samples were measured at 303K using an automatic vapor adsorption analyzer. The photocatalytic activity for the decomposition of

benzene in air was evaluated using a flow system shown in Figure 1 and was preferred over using a batch system due to the high benzene adsorption capacities which were observed. A blacklight bulb of 4W was located in the reactor, and humidified air was mixed with benzene vapor. Aerogel samples or conventional titania (Degussa P25) were mixed with 20g glass beads then placed in the photoreactor. It was found that aerogels samples showed larger adsorption capacities than P25. Titania-impregnated silica aerogels appeared suitable for use as adsorbents with photocatalytic properties, as it was found that after irradiation, the degree of removal of benzene was continuously increased and benzene adsorbed on the aerogels was confirmed to be decomposed as CO<sub>2</sub>. This shows potential for an adsorbent with a self-cleaning function that can adsorb VOCs in the dark and decompose them in the presence of light without the necessity of supplying power (Yoda et al. 2000).

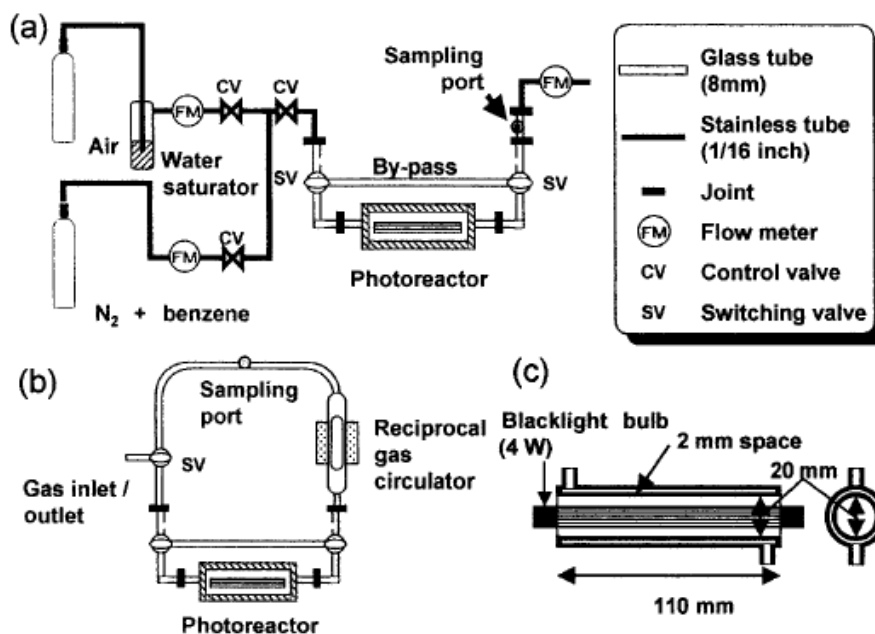


Figure 2. Schematic of Yoda 2001 PCO set-up

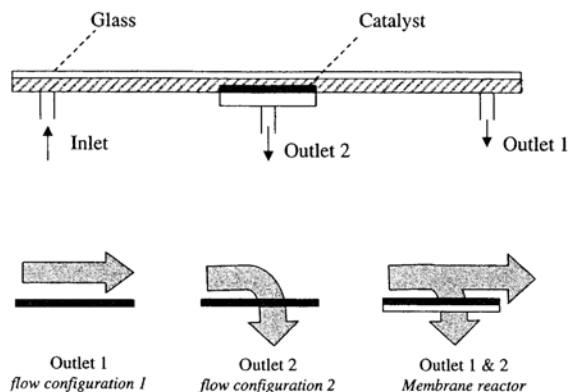
Yoda et al. (2001) discussed the large capacities for benzene adsorption and high photocatalytic activity for its decomposition in the adsorbed state. The degree of benzene removal seemed to depend on the crystallinity of the titania while the adsorption capacity of benzene depended on the silica matrix. It was pointed out that air pollution by toxic chemicals such as volatile organics (VOCs) could be potentially harmful to human health, but may be removed by either adsorption using a porous material or decomposition using a photocatalyst. Obviously, it would be most practical to use a material with both of these properties, such as a titania-silica aerogel.

In Yoda et al. (2001), adsorption and decomposition isotherms of benzene vapor on Yoda's aerogel samples were measured at 303K using an automatic vapor adsorption analyzer. The photocatalytic activity for the decomposition of benzene in air was evaluated using a flow type reactor. The test gas was prepared by mixing CO<sub>2</sub>-free humidified air with benzene. The sample was mixed with glass beads and placed in the photoreactor, using a black light bulb as a light source, very much like the previous article. It was found that the concentration of CO<sub>2</sub> produced by the decomposition of benzene increased rapidly at first then decreased gradually to certain values after thirty minutes. The decrease probably occurred due to the benzene adsorption before irradiation was rapidly decomposed in the initial stage. Both the efficiency of benzene decomposition and CO<sub>2</sub> production increased with increasing crystallinity of titania. A combination of silica and titania systems were recommended to be advantageous in improving the adsorption capacity and probably to decompose the intermediate products completely through to CO<sub>2</sub> (Yoda et al. 2001).



Cao et al. (2006) found titania aerogel powders to be more active than Degussa P25 titania for the photocatalytic decontamination of organic pollutants in water. They performed photocatalytic oxidation reactions at room temperature in a flat-plate photoreactor. The VOCs including isopropyl alcohol and trichloroethylene were fed by a syringe pump and mixed with dry synthetic air. Fluorescent black lamps were used to irradiate the catalyst and a gas chromatograph analyzed the reacted gases. Three catalysts were tested; Degussa P25 titania mixed with silica aerogel, Degussa P25 titania alone, and a silica aerogel impregnated with Degussa P25 powder. It was found that only the titania-silica aerogels containing anatase titania prepared by ethanol supercritical drying were active for the PCO reactions. It was found that complete conversion of isopropyl alcohol was observed with no other byproducts detected by gas chromatography. The catalyst was stable and the experimental data was reproducible. They found that aerogels with low density, high permeability, large surface area and pore size were attractive materials for gas filtration, VOCs adsorption and remediation (Cao et al. 2006).

Maira et al. (2003) discusses the importance of photocatalytic oxidation more in depth than previous articles. This article evaluated the performance of a flat-plate photoreactor using nanostructured  $\text{TiO}_2$  catalyst and a hybrid zeolite- $\text{TiO}_2$  membrane catalyst for PCO of gas-phase trichloroethylene.



**Figure 3. Maira et al. (2003) schematic diagrams of the multipurpose reactor.**

The photocatalytic reactor used for the gas-phase PCO of VOCs contains an inlet and two outlet ports, a recess for the catalyst plate and two sets of machined baffles. One outlet is at the opposite end of the reactor from the inlet and the other is at the bottom of the catalyst recess. The gas flow is parallel to the catalyst plate when the first outlet is used, but is forced through the porous catalyst plate when the second outlet is used. The photocatalyst was illuminated by five fluorescent black lamps and the outlet gases were separated and analyzed using a gas chromatograph equipped with thermal conductivity and flame ionization detectors.

A previous report suggested that the use of a membrane in hybrid photoreactor units can be advantageous for the degradation of organic pollutants in water. It was determined that the final steady-state value for trichloroethylene degradation and mineralization is significantly higher in the hybrid membrane-catalyst system. Both the trichloroethylene conversion rate and CO<sub>2</sub> selectivity were better with the hybrid membrane-catalyst than results obtained with the catalyst plate (Maira et al. 2003).

Another group tested the photocatalytic activities of S-doped TiO<sub>2</sub> material under visible light (Ohno et al. 2004). Photocatalytic activity was estimated by measuring the

decomposition rate of methylene blue in an aqueous solution containing 100mg of the TiO<sub>2</sub> photocatalyst, which was either S-doped TiO<sub>2</sub> or pure TiO<sub>2</sub> powder. Their results show that S-doped TiO<sub>2</sub> material is able to photocatalytically decompose methylene blue under visible light. These materials may be extremely useful in cleaning up pollutants in air and water, and the faster process that RSCE provides to fabricate titania-silica aerogels would be beneficial.

Cao and Gao, et al. (2000) studied deactivation and regeneration of the photocatalytic oxidation of toluene on nanoscale TiO<sub>2</sub> catalysts. This study found that severe deactivation of TiO<sub>2</sub> catalyst is due to the accumulation of partially oxidized intermediates on active sites, for example, benzaldehyde and benzoic acid. Deactivation of photocatalysts has been found to be a disadvantage of PCO in practice, especially for the oxidation of aromatics. Oxygen-bearing compounds can cause irreversible loss in the photoactivity of TiO<sub>2</sub> catalysts. The apparatus used was a glass plate photocatalytic reactor under high flow rates on the order of 3.6 l/min and low concentrations of toluene (<20%). The oxidation rates of toluene were based on the difference in toluene concentrations before and after UV illumination. No intermediate products were detected in the effluent, although they were identified on the surface of used catalysts. The catalyst that demonstrated the highest catalytic activity (0.52  $\mu\text{mol/h}\cdot\text{cm}^3$ ) was prepared using a sol-gel method and calcined at 350°C and found to be a nanoscale crystal with a 7.0 nm particle size. However, this oxidation rate was found to decrease significantly over time to around 0.1  $\mu\text{mol/h}\cdot\text{cm}^3$ . It was also found that the oxidation rate was highest in less than 10% relative humidity and decreased with increasing humidity. Regeneration of

deactivated catalysts was studied and found to be most suitable at a temperature of 420°C and occurs when the chemisorbed carbon species are burned out in air.

Maira et al. (2001) researched gas-phase photo-oxidation of toluene using nanometer-size TiO<sub>2</sub> catalysts. In this system, a continuous flow photoreactor was used. The catalyst was a concentrated solution of TiO<sub>2</sub> nanoparticles which was painted onto a glass tube. Four 210 mm long 6W fluorescent lamps were placed around the photoreactor inside a box with reflective walls. Toluene was added to the system using a syringe pump. Once added, the vaporized toluene was mixed with either wet or dry oxygen. Tests were performed at ambient pressure and 343K using 100mg of TiO<sub>2</sub> catalyst. Different oxygen flow rates (50, 100, and 300 ml/min) and amounts of toluene concentrations (0.06, 0.14, 0.15 mmol dm<sup>-3</sup>) were tested. A GC/MS was used to analyze the outlet gas mixture. It was determined that the reaction rate of toluene increases with both flow rate and toluene concentration. Research showed that water stabilizes the TiO<sub>2</sub> catalyst during the PCO of toluene. Another finding was that higher conversions obtained by decreasing the particle size from 20nm to 16 and 11nm are mainly due to the increase in surface area, but was not the case for 6nm catalyst. The products of toluene PCO for the 6nm TiO<sub>2</sub> catalyst were carbon dioxide and water, indicating a complete breakdown of toluene, but this did not occur with the other catalysts, which produced benzaldehyde.

Photocatalytic oxidation using aerogels has been extensively researched and proven successful. It has proven the ability to break down pollutants such as benzene, trichloroethylene, methylene blue, 2-propanol, adamantane, and toluene in aqueous solutions or air. Many different methods and reactors have been used, such as flat-plate

reactors or flow-type reactors. A summary of the previous results found can be seen below in Table 1. This information has been extremely useful in designing research to be done to test the photocatalytic oxidation of titania-silica aerogels that have been fabricated using the rapid supercritical extraction method.

<i>Author</i>	<i>Year</i>	<i>Chemical removed</i>	<i>Working fluid</i>	<i>Degree of success</i>
Méndez-Román	1998	toluene	air	Gas-phase oxygen is necessary to complete PCO
Yoda	2000	benzene	air	1500ppmv benzene decreased to ~100ppmv
Maira	2000	trichloroethylene	air	PCO activity depends on crystal size of TiO <sub>2</sub>
Cao	2000	toluene	air	No intermediate products detected in the effluent
Maira	2001	toluene	air	complete mineralization of toluene
Maira	2003	trichloroethylene	air, water	20% complete mineralization of TCE was seen
Ohno	2004	methylene blue	water	higher rates of methylene blue decomposition
Cao	2006	isopropyl, TCE	air	removal efficiency TCE:9.7% IPA:10.1%

**Table 1. Summary of Literature Review findings**

The goal of this project was to design and build a flow through photocatalytic oxidation test apparatus to test the photocatalytic oxidation abilities of titania-silica fabricated using the Rapid Supercritical Extraction method and test the ability of titania-silica aerogels to perform photocatalytic oxidation. This report presents the results of that study. Detailed procedures on how titania-silica aerogels are fabricated and characterized are included, as well as preliminary characterization results. Testing of the degradation of methylene blue in an aqueous solution using titania-silica aerogels is presented, as well as the design and building of the toluene photocatalytic oxidation test apparatus and initial results.

## CHAPTER 2: TITANIA-SILICA AEROGEL PROCEDURES

Previous research was done at Union College to develop a method for fabricating titania-silica aerogels using the Rapid Supercritical Extraction Method. Two recipes were tried, with very different results, but the surface area and density characteristics demonstrate that each material fabricated is, in fact, an aerogel. The first recipe was from Yoda et al. (2000). In this method, a silica wet gel was fabricated and then impregnated with a titanium isopropoxide and acetylacetone solution. After it was supercritically dried using the RSCE method, a titania-silica aerogel resulted with densities on the order of  $0.1 \text{ g/cm}^3$  and BET surface areas on the order of  $600 \text{ m}^2/\text{g}$ . Although the characteristics of these aerogels were desirable, the fabrication process took about a week, which was not ideal. At this point, the second recipe was tried (Brown 2010).

The second recipe used was the “rapid” method (Brodzik et al. 2008). The recipe for 20% titania aerogels was used. Titanium isopropoxide, tetraethyl orthosilicate, ethanol, water, 0.363M hydrochloric acid and ammonia were used in the fabrication. The molar ratio of TEOS: EtOH: H<sub>2</sub>O:HCl:TIP was 0.02:0.51:0.08:0.274x10<sup>-3</sup>:0.0208. After the solution was mixed, it was poured into a mold and placed into the hot press for processing. Brodzik aged the precursor solution for 18 hours before drying at the supercritical level. It was determined in previous research that this was not necessary, so the precursor solution was processed immediately after mixing. Details about the recipe used and hot press process can be seen below.

### Precursor Solution

This method uses titanium isopropoxide (TIP), tetraethyl orthosilicate (TEOS, Aldrich,  $\geq 99\%$ ), ethanol, water, 0.363M hydrochloric acid, 1.5M ammonia catalyst. The molar ratio of TEOS: EtOH: H<sub>2</sub>O:HCl:TIP is 0.02:0.51:0.08:0.274x10<sup>-3</sup>:0.0208, respectively. Quantities can be found in Table 2. The first step is to mix TEOS with TIP. The second step is homogenization with a magnetic stirrer for 5 minutes. Then reagents are added: ethanol, water and the HCl solution. Next is homogenization with a magnetic stirrer for 15 minutes. Following this is the addition of more reagents; water, ethanol and 1.5M ammonia solution. The solution is then homogenized for five more minutes before being poured into a mold then placed into the hot press.

	Chemical	Quantity (mL)	Mass (g)	Molar quantity (moles)
<b>Step 1</b>	TEOS	4.5	4.2	0.02
	TIP	0.94	0.90	0.0032
<b>Step 3</b>	EtOH	29.91	23.6	0.512
	H <sub>2</sub> O	0.97	1.45	0.08
	0.363M HCl	0.48	0.05	0.00017
<b>Step 5</b>	water	0.24	0.24	0.0128
	EtOH	2.66	2.1	Not specified
	1.5M NH <sub>3</sub>	0.42	0.38	Not specified

**Table 2. The quantities of chemicals used in the second recipe for a 20% Ti aerogel [1].**

Each batch was given a letter which was preceded by “LB TiSi<sub>2</sub>,” meaning that it was a titania-silica aerogel fabricated using the second recipe, by Lauren Brown. Some batches had variations in recipe or processing, which can be seen in the table below.

Sample	Fabrication Variances
G	less mixing
H	less mixing
I	less mixing
J	standard fabrication
K	30% Ti

L	standard fabrication
M	2x faster heat
N-20%	3x faster heat
N-30%	30% Ti, 3x faster heat
O-20%	3x faster heat, 2x catalyst
O-30%	30% Ti, 3x faster heat, 2x catalyst
P	2x heat, impregnated glass beads
Q	2x heat, impregnated glass beads
R	2x heat, impregnated glass beads
S	2x heat
T	2x heat
U	2x heat, a few wells w/ beads
V	2x heat, a few wells w/ beads

**Table 3. The processing differences for each batch of titania-silica aerogel fabricated.**

The variation “less mixing” means that the third time mixing was only one to two minutes long instead of the specified five minutes. For the variation “faster heat,” the heat rate was increased, but the dwell time was also increased so that the second step always took the same amount of time, it just reached the final temperature faster during some batches than others. Details about the faster heating rate are below.

### **Rapid Supercritical Extraction Process**

After the precursor solution or gel was prepared, it was poured or placed into a cold-rolled steel nine well mold with a diameter of 1.25 inches. A piece of kapton and graphite gasket was placed on top of the mold to seal the mold. The kapton was used to prevent the gasket from sticking to the mold. The mold was placed in a 50-ton Tetrahedron hot press to be fabricated by the Rapid Supercritical Extraction (RSCE) process.

Before the precursor solution is poured into the hot press, a ten minute program is run to seal the bottom of the mold with a layer of kapton sandwiched between the mold



and graphite with a force of 10 kips. After the pre-process is complete, the precursor does not leak when it is being poured in and the program can begin. The hot press was programmed to provide high temperature and pressure, taking the solvent in the pores of the wet sol-gel past the supercritical point of the solvent. The pressure was then released and the solvent escaped, ideally leaving an aerogel. The hot press program used is seen in Table 4.

<b>Step</b>	<b>Temperature (°F)</b>	<b>Temp rate (°/min)</b>	<b>Force (kips)</b>	<b>Force rate (kip/min)</b>	<b>Dwell time</b>
<b>1</b>	90	200	48	600	2 min
<b>2</b>	575	3	48	10	2 hour
<b>3</b>	575	200	1	1	30 min
<b>4</b>	90	8	1	600	30 sec
<b>5</b>	end				Total time: 7 hours

**Table 4. The hot press program used to fabricate titania-silica aerogels via the RSCE method.**

Once the hot press finished the program, it opened. A titania-silica monolith was left in the mold. This monolith could then be characterized. For batches M, N, and O, a faster heating rate was utilized during step 2. Batch M had a temperature rate of 6°/minute with a dwell time of 3 hours and 20 minutes, so that the step 2 with faster heating took the same amount of time as the original step 2. Batches N and O had an even faster heating rate of 9°/minute with a dwell time of 3 hours and 46 minutes during step 2.

### **Characterization**

The fabrication and characterization details for each batch of titania-silica aerogels were documented in a characterization sheet (found in Appendix A). Each batch is named a successive letter of the alphabet, following “TiSi2” which stands for titania-

silica aerogels, second recipe, since there was a first recipe which was discussed previously. A picture is taken of each batch of monoliths. Qualitative results are documented, including color, whether or not shrinkage occurred, relative degree of monolithicity and relative texture.

Bulk density is estimated by measuring the mass of one sample from each batch and assuming the volume completely filled the well of the mold. Skeletal density is measured using a Micromeritics AccuPyc 1330 pycnometer. Each sample was purged 99 times at a pressure of 18.5 psi before testing.

BET surface area and BJH pore distribution were taken using a TriStar 3000 Gas Adsorption System (Micromeritics). The sample was crushed using a mortar and pestle and transferred to a test tube that was massed before a sample was added, after a sample was added and after being degassed. The aerogel powder proved to have static, making it difficult to work with. This was remedied using an antistatic wrist strap that grounds the wearer. Each sample was degassed for 2 hours at 90°C then 2 hours at 200°C before being analyzed. The BJH pore distribution was analyzed by a 39 point adsorption, followed by a 37 point desorption.

X-ray diffraction was used to analyze the degree of crystallinity in the titania-silica aerogels. Powder diffraction was used to analyze TiSi2L with settings of 45kV, 35mA, and a scan rate of 0.6 2 $\theta$ /minute. Results were then compared against the Brodzik 2008, as well as Imai et al. 1999 to determine composition. Fourier transform infrared spectroscopy was done to look at the percent transmittance in the range of 4000-500 cm<sup>-1</sup>.

Energy dispersive X-ray spectroscopy was also used for the chemical characterization of a few samples. The samples were scanned using the scanning electron

microscope (SEM) and then a certain area of the sample analyzed. A plot of the relative amounts of each element, as well as a color-coded image indicated where each element was located in the specified area of the sample were the results of this analysis.

## Aerogel Results

### *Qualitative*

Each batch of titania-silica aerogels fabricated is white, squishy, and monolithic. Shrinkage was observed in the 30% Ti batch (TiSi2K). The gels have been monolithic until removed from the mold and placed into sample containers. They are fragile enough that they fall apart unless extreme caution is exercised when touching them. Some batches are more monolithic than others. The batches that fell apart easily were denoted as more powdery.

A picture of a few of the fabricated monoliths from various batches can be seen below in Figure 4.

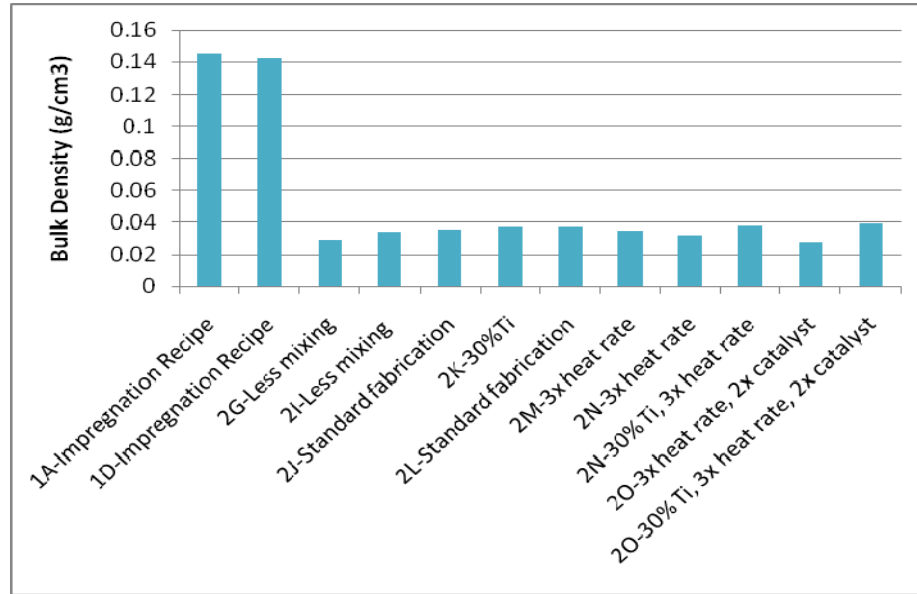


**Figure 4. Titania-silica monoliths fabricated using the Rapid Supercritical Extraction method.**

## Bulk Density

Bulk density was determined by assuming the monolith filled the well of the mold, a volume of  $5.999 \text{ g/cm}^3$ . The monolith was massed and density was calculated.

Bulk density results can be seen in Figure 5. Samples 1A and 1D were fabricated in previous research using a different recipe.



**Figure 5. Bulk densities of titania-silica aerogel samples from various batches.**

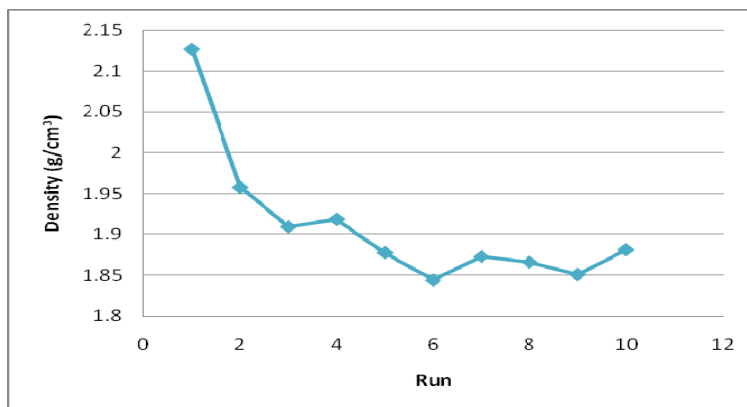
Batch	Fabrication Details	Bulk Density (g/cm <sup>3</sup> )	Skeletal Density(g/cm <sup>3</sup> )	BET Surface Area (m <sup>2</sup> /g)
1A	Impregnation	0.145	n/a	649
1D	Impregnation	0.142	n/a	641
2G	Less mixing	0.029	1.84	680
2I	Less mixing	0.034	2.83	420
2J	Standard fabrication	0.036	2.37	340
2K	30% Ti	0.037	2.21	250
2L	Standard fabrication	0.037	2.44	419
2M	2x faster heat	0.035	2.39	n/a
2N-20%	3x heat rate	0.032	2.52	263
2N-30%	30% Ti, 3x heat rate	0.038	2.62	273
2O-	3x heat rate, 2x catalyst	0.028	2.6	181

20%				
2O-30%	30% Ti, 3x heat rate, 2x catalyst	0.039	n/a	218

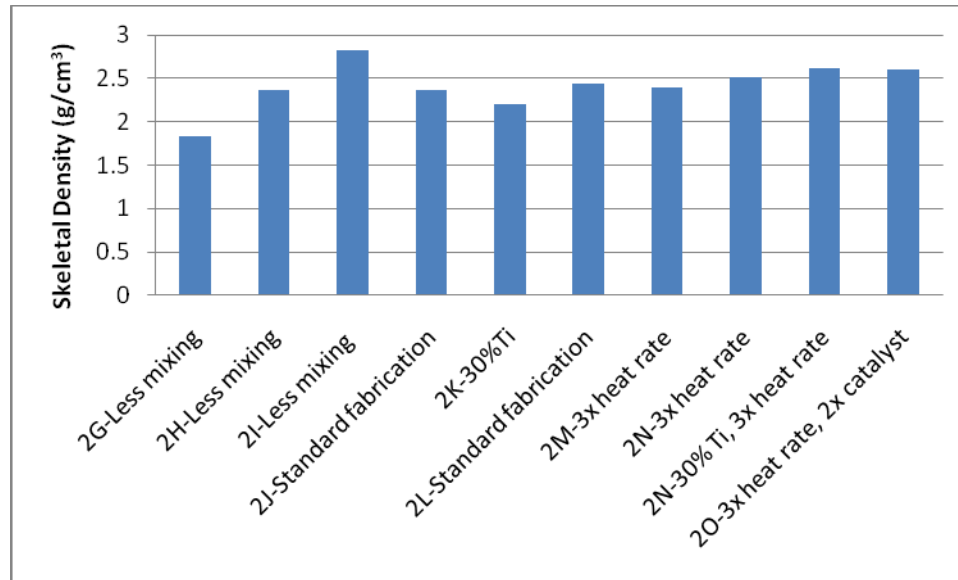
**Table 5. Characterization details and values for selected batches.**

### ***Skeletal Density***

Each skeletal density sample was run 6-10 times, as it was noted that the first few runs resulted in high values likely due to the presence of water vapor. After multiple runs, the values obtained evened out. The values shown are the average value for the sixth run, since each sample was analyzed at least six times. This trend is demonstrated in Figure 6. Skeletal density results can be seen in Figure 7.



**Figure 6. Average skeletal density of batch TiSi<sub>2</sub>G shown for 10 runs.**



**Figure 7. Skeletal Densities of titania-silica aerogel samples from various batches.**

### ***BET Surface Area***

BET surface area results can be seen in Figure 8. Samples that were fabricated using the Impregnation Recipe were measured in previous research (Yoda et al. 2000). The samples fabricated using the Impregnation Recipe have higher surface area, likely due to higher percentages of silica. The samples fabricated by the standard fabrication method and method with less mixing seem to have higher percentages of silica, since they have higher surface areas. The faster heating methods and methods fabricated with more titania have lower surface areas, seemingly because titania is more equally distributed throughout the sample. Error bars show 10% standard error.

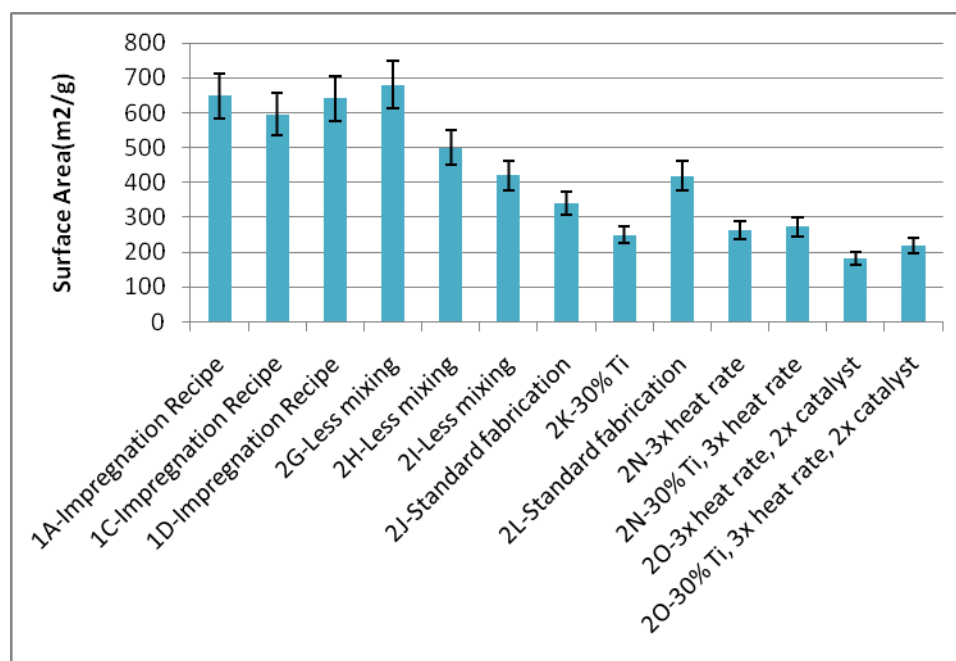
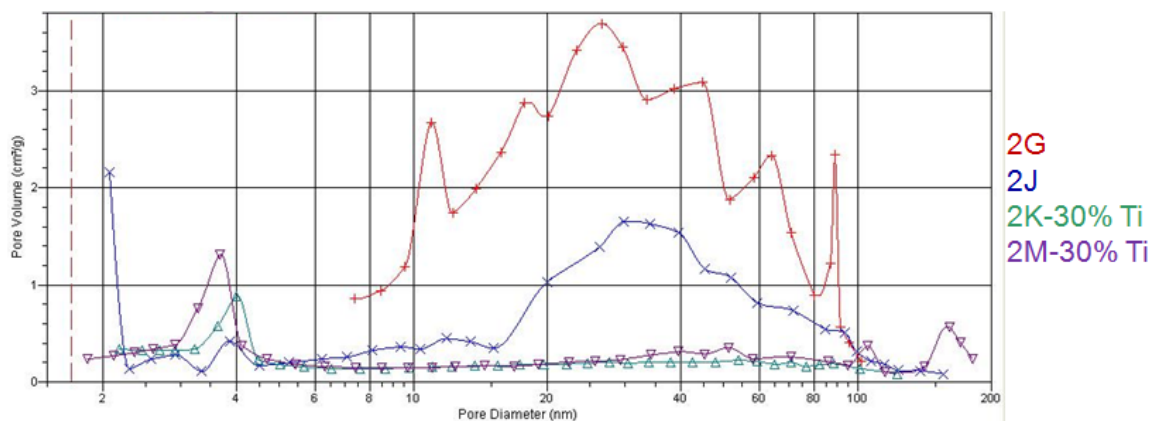


Figure 8. BET Surface Areas of titania-silica aerogel samples from various batches.

### ***BJH Pore Distribution***

BJH pore distribution results can be seen in Figure 9. The sharp spikes may be false points, the general trend of each sample is what can be gained from this plot. The larger, round peaks are more representative of silica aerogels that have higher pore volumes (2G,2J). The flat, straight lines are more representative of titania aerogels which have larger ranges of pore diameters, but less pore volume (2K-30%, 2M-30%).

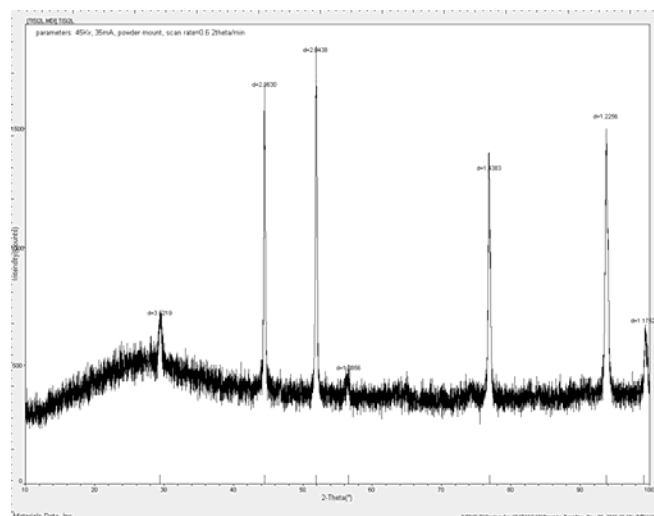




**Figure 9. BJH Pore Distribution plots for titania-silica aerogels from various batches.**

## *X-Ray Diffraction*

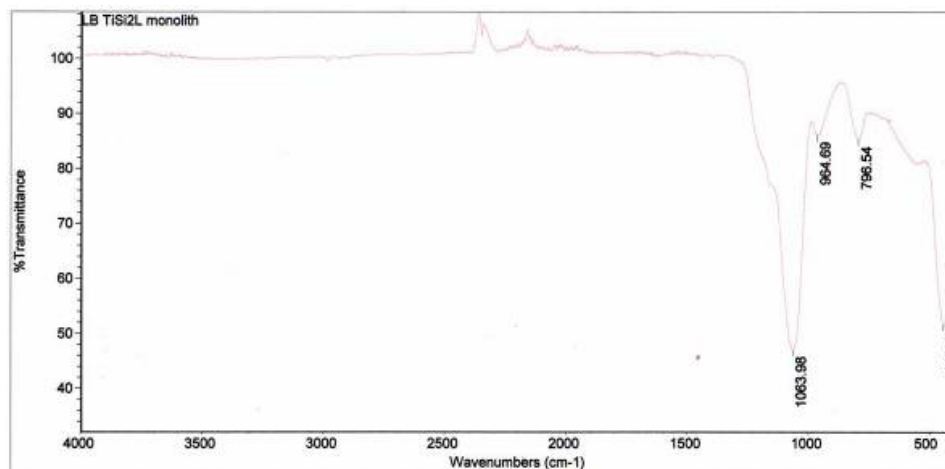
The XRD analysis for sample TiSi2L can be seen in Figure 10. The four larger peaks and last peak on the right are thought to be caused by the sample holder. However, the first two smaller peaks ( $d=3.52$ ,  $d=1.88$ ) are most likely anatase titania. This hypothesis is confirmed by similar peaks in the Brodzik and Imai references.



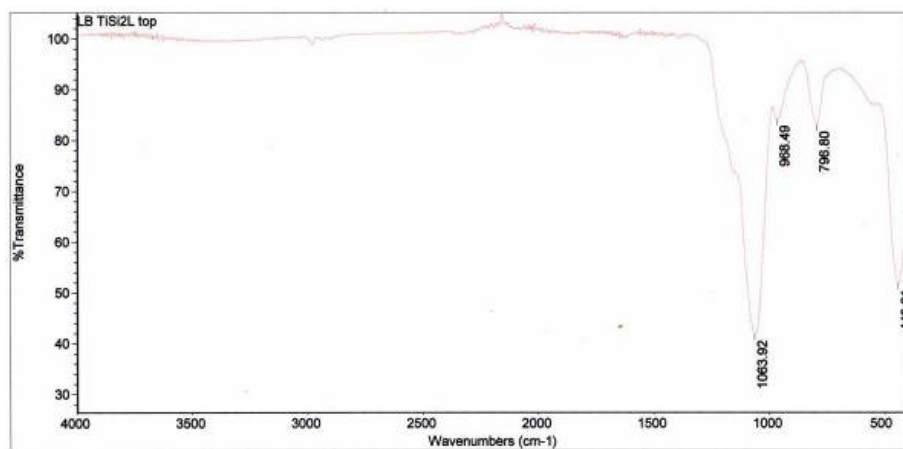
**Figure 10. X-Ray Diffraction Results for TiSi<sub>2</sub>L.**

### ***FTIR Analysis***

Percent transmittance of the lower portion of the TiSi2L monolith and the top portion of TiSi2L monolith are seen below in Figures 11 and 12, respectively. This sample was chosen particularly because the top portion of the TiSi2L monolith looked distinctly like a titania aerogel while the lower portion looked distinctly like a silica aerogel. After some discussion with peers and professors who profess knowledge about FTIR spectra, there is negligible difference between comparable silica spectra and titania-silica spectra.



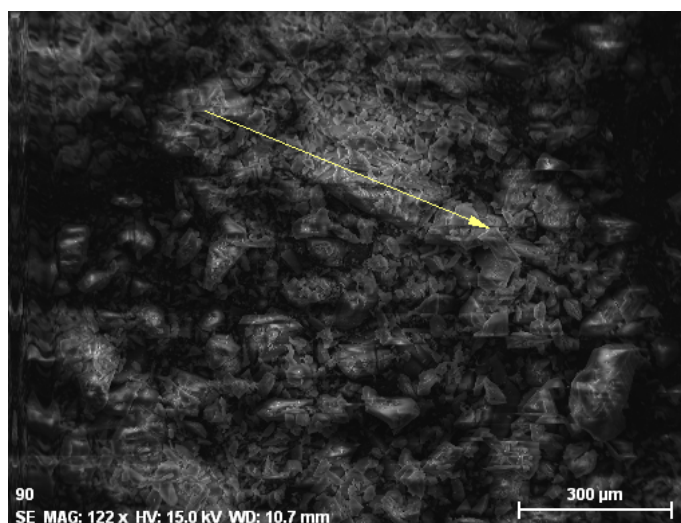
**Figure 11. FTIR spectra of the bottom part of TiSi2L sample.**



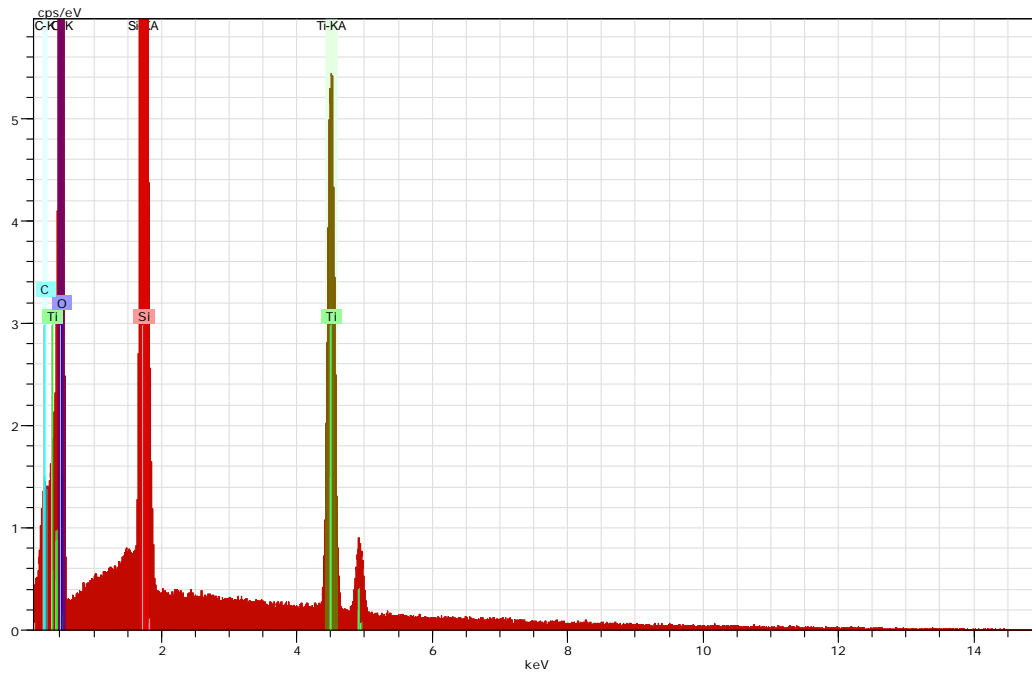
**Figure 12. FTIR spectra of the top part of TiSi2L sample.**

### ***Energy Dispersive X-ray Spectroscopy***

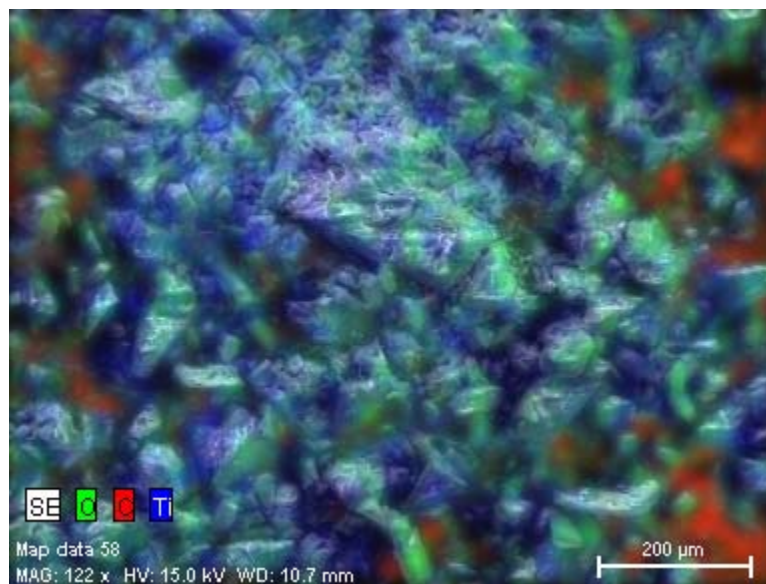
Three samples were analyzed using EDX. One sample was fabricated using the first recipe used (impregnation recipe), the second sample was 30 wt% titania (all of the other samples, unless specified are 20 wt%), and the third sample was fabricated using the standard method of titania-silica fabrication. The arrow in each SEM image indicates the area analyzed.



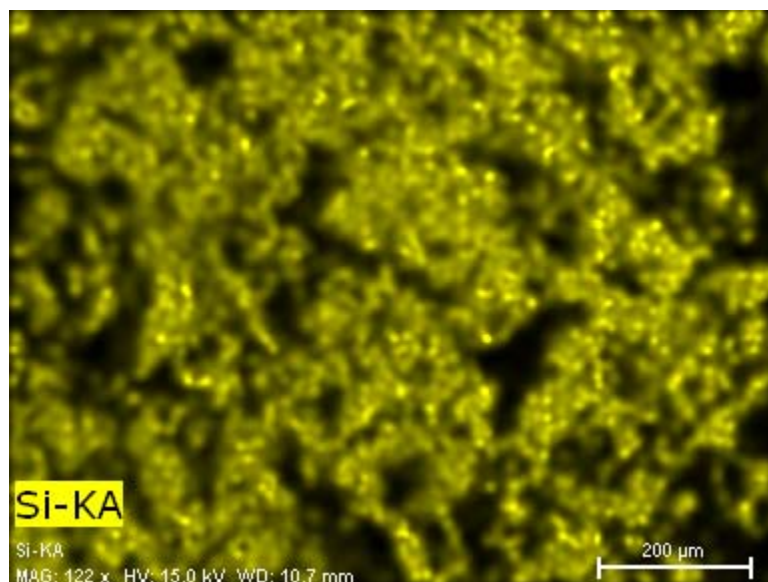
**Figure 13. SEM image of sample TiSi1F used in EDX analysis.**



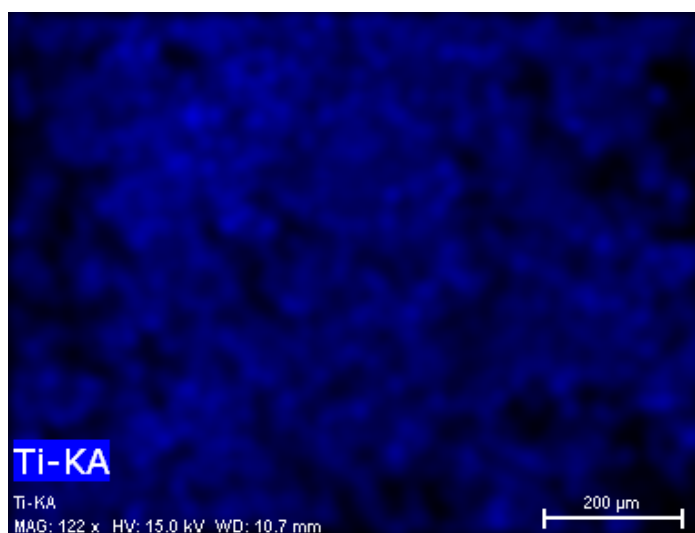
**Figure 14. EDX chemical composition plot for sample TiSi1F.**



**Figure 15. EDX chemical composition map of sample TiSi1F.**



**Figure 16. EDX chemical composition map of silica present in sample TiSi1F.**



**Figure 17. EDX chemical composition map of titania present in sample TiSi1F.**

It was expected that there would be a large amount of titania present in this sample, relative to the other two samples, since it was made using the impregnation method. Additionally, this analysis verified that the titania seemed to be relatively well distributed throughout the sample. The second sample analyzed was TiSi2K which was 30 wt% titania.

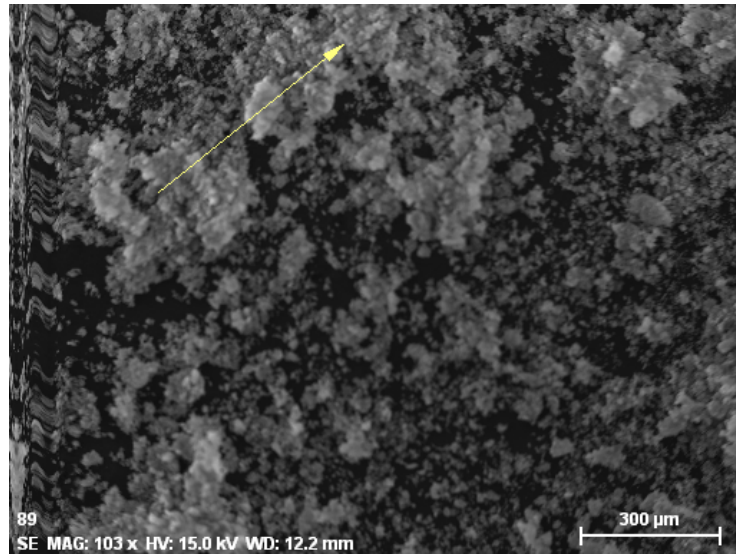


Figure 18. SEM image of sample TiSi2K 30% used in EDX analysis.

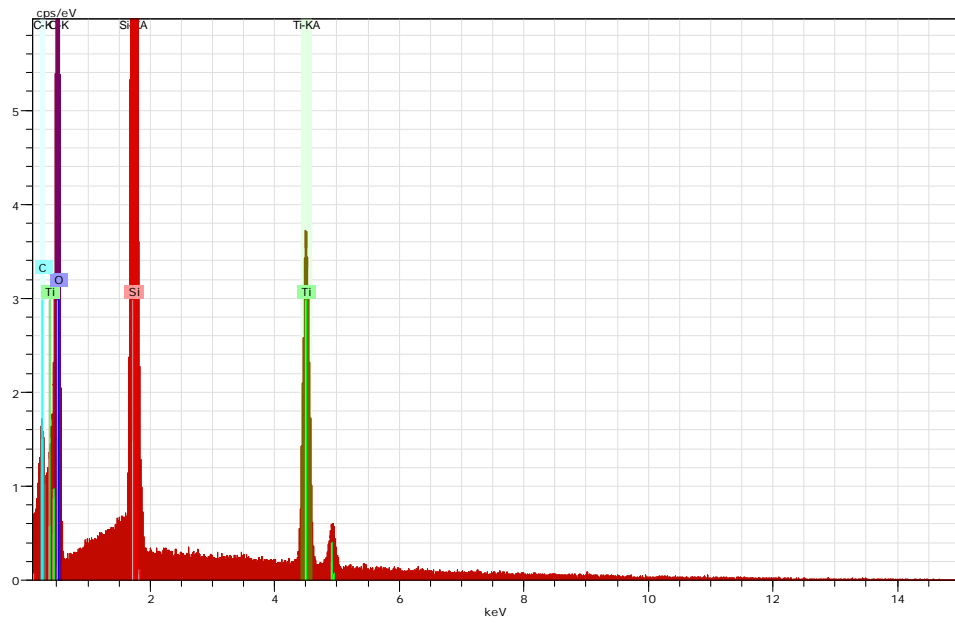
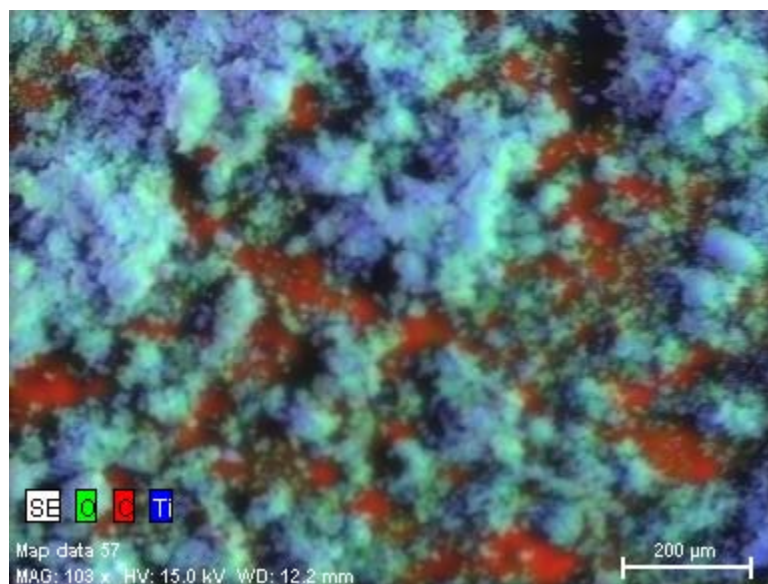
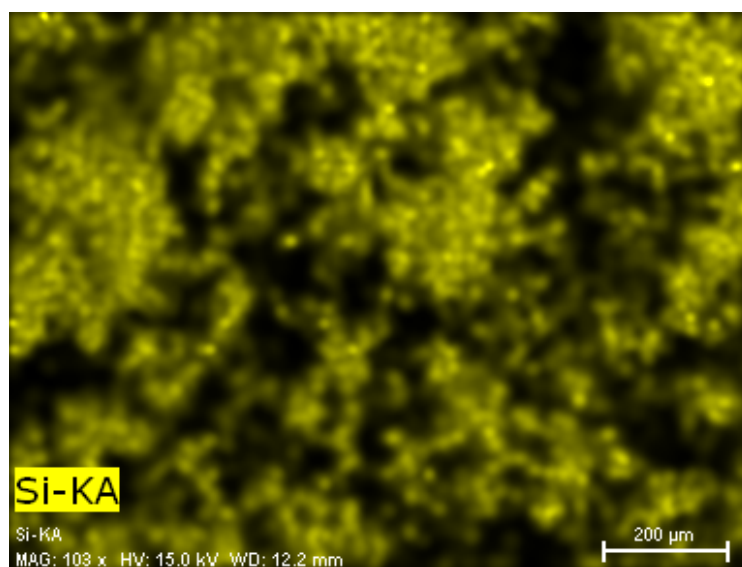


Figure 19. EDX chemical composition plot for sample TiSi2K 30%.

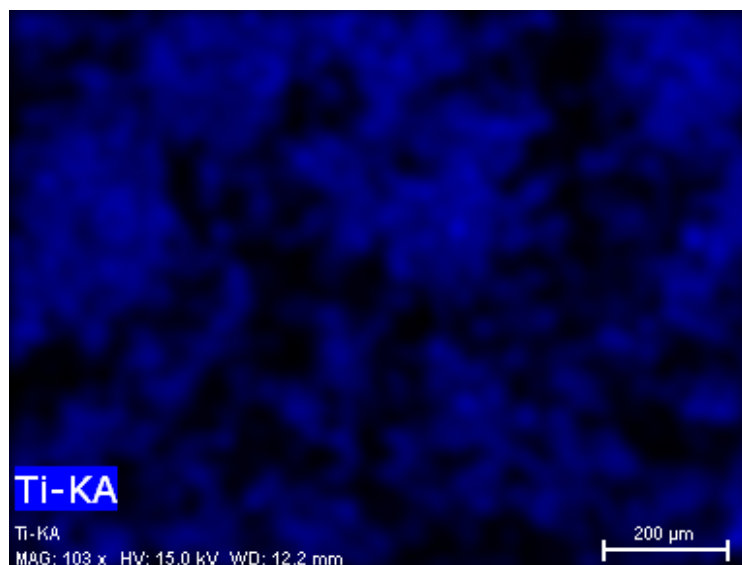


**Figure 20. EDX chemical composition map of sample TiSi<sub>2</sub>K 30%.**



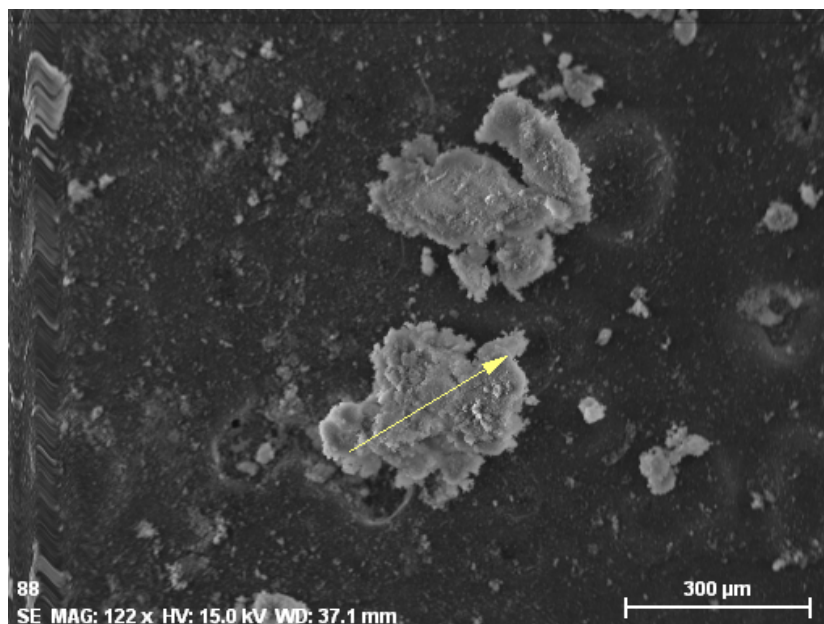
**Figure 21. EDX chemical composition map of silica present in sample TiSi<sub>2</sub>K 30%.**





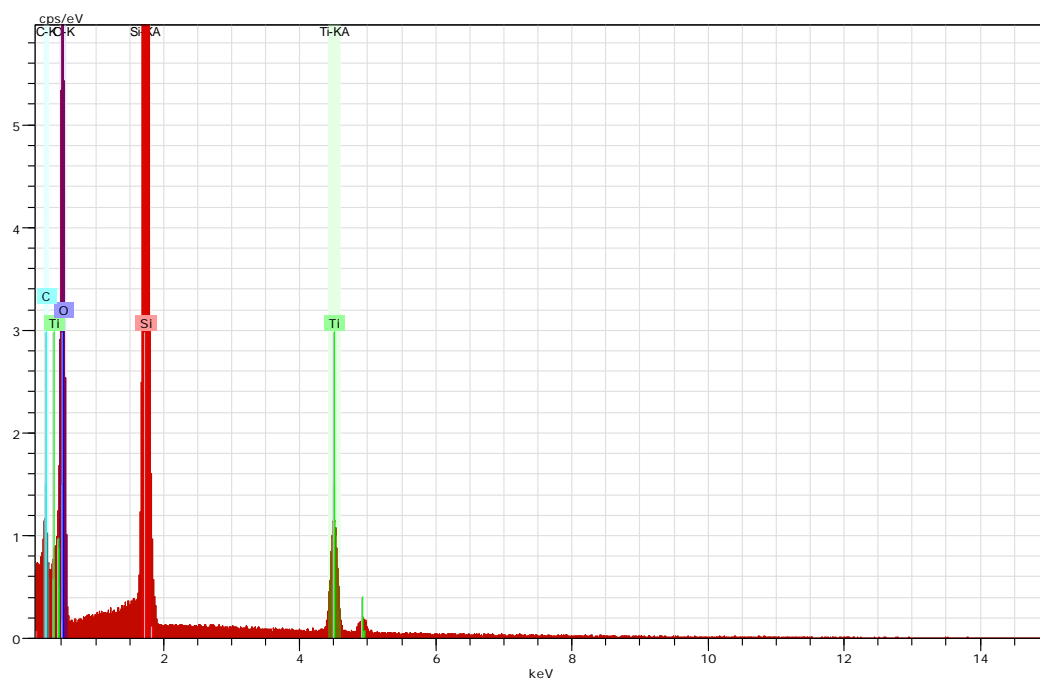
**Figure 22. EDX chemical composition map of titania present in sample TiSi2K 30%.**

The analysis on this sample showed similar results to sample TiSi1F, however there was relatively less titania. Although there was a higher percent weight titania in TiSi2K, the method of fabrication was different which could explain the difference. Additionally, a reasonably even distribution of titania was seen throughout the analyzed portion of the sample. The results from a third analysis, sample TiSi2S are shown below.

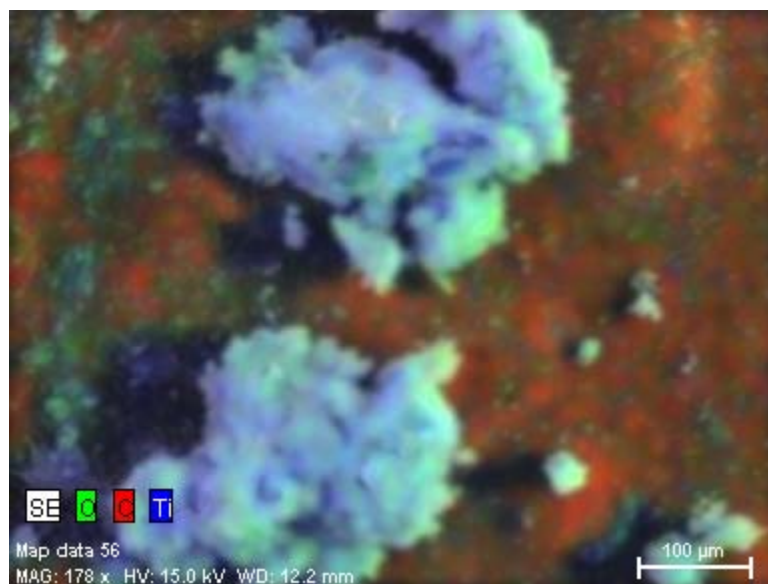




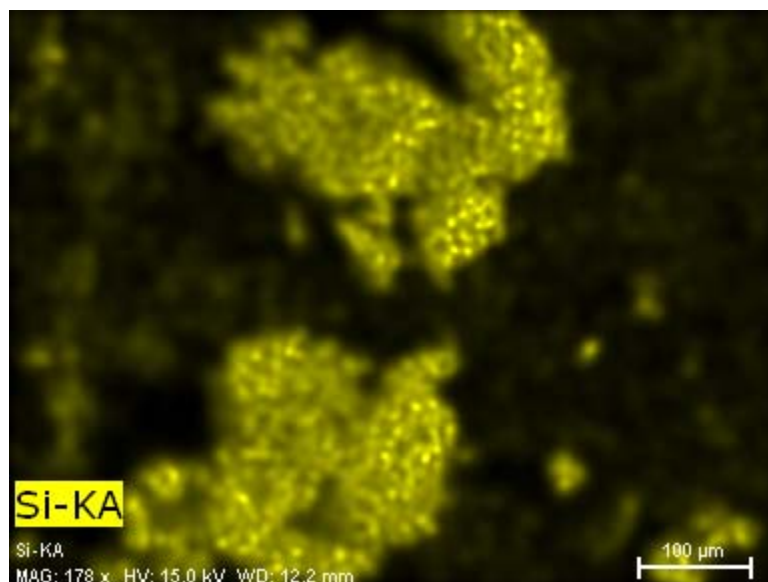
**Figure 23. SEM image of sample TiSi2S used in EDX analysis.**



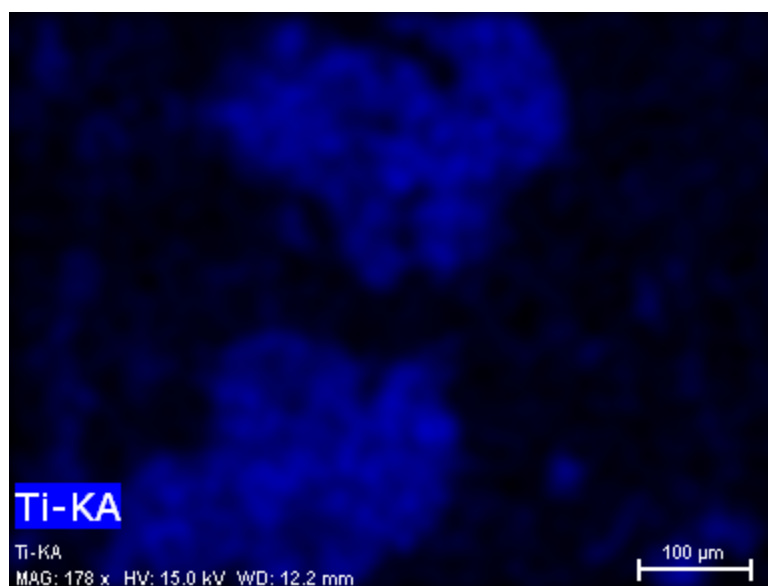
**Figure 24. EDX chemical composition plot for sample TiSi2S.**



**Figure 25. EDX chemical composition map of sample TiSi2S.**



**Figure 26. EDX chemical composition map of silica present in sample TiSi2S.**



**Figure 27. EDX chemical composition map of titania present in sample TiSi2S.**

The analysis performed using EDX for sample TiSi2S showed similar results to the previous samples. Titania seemed to be distributed throughout the sample. There was also a relatively lower level of titania than the other two samples, which would be expected since it was fabricated using the rapid method with the standard amount of titania, as compared with 30 wt% with sample TiSi2K.

## CHAPTER 3: PHOTOCATALYTIC OXIDATION OF METHYLENE BLUE

### **Methylene Blue Testing Procedures**

Initial experiments were performed to test the photocatalytic oxidation abilities of titania-silica aerogels. The first simple test investigated the photodegradation of methylene blue when exposed to 24 hours of visible light (Maira et al. 2003).

An aqueous solution of methylene blue at concentration  $50 \times 10^{-3}$  mol/L was made. Five milliliters of the aqueous solution was pipetted into a test tube. Into another test tube was placed five milliliters of the aqueous methylene blue solution, as well as approximately 91.5mg of titania –silica powder from the TiSi2I batch. Both test tubes were covered with parafilm and then placed in a clear beaker under a window for 24 hours. It should be noted that it was particularly rainy during these 24 hours, so it is doubtful that the samples were exposed to direct sunlight at all.

A second test was performed using a solar simulator. Four samples of titania-silica aerogels from different batches (2I, 2K, 2L, 2M 30%) were tested. Four 10mL aqueous solutions with concentrations of 50 $\mu$ M were prepared. Absorbance of one solution was measured using a spectrophotometer. Two spatulas full of sample were then added to the solution. Test tubes were shaken until the sample seemed to be in suspension. The tubes were placed in the solar simulator for thirty minutes at 765 W/m<sup>2</sup>. After thirty minutes, samples were removed and spectra were taken.

Another test was performed using the solar simulator. Six samples from aerogel batch TiSi2O-30%Ti. Two samples, one with an aqueous methylene blue solution (sample A) and another with the same aqueous methylene blue solution and 0.03g of

aerogel sample (sample B), were covered in aluminum foil as to not be exposed to light to test whether the exposure to light was actually causing a degradation of methylene blue. The other four test tubes were exposed to UV and visible light in the solar simulator. The first of these four samples was aqueous methylene blue solution alone (sample C). The second sample was aqueous methylene blue solution with 0.03g of aerogel sample (sample D). The third was aqueous methylene blue solution with 0.015g of aerogel sample (sample E). The fourth and last sample was aqueous methylene blue solution with 0.008g of aerogel sample (sample F). All six samples were placed in the solar simulator to be exposed to  $756\text{W/m}^2$  of light for 45 minutes. Two base spectra were taken, and spectra were then taken at fifteen minute intervals. Results were also documented with pictures.



**Figure 28. Solar Simulator used in testing photodegradation of methylene blue.**

## Methylene Blue Results

The initial set-up and resulting test tubes can be seen in Figures 29 and 30, respectively. Each sample had 5mL of a 50 mmol/L aqueous methylene blue solution. The sample on the right also had about 0.09g of TiSi2I powdered sample in the test tube. Both test tubes were exposed to natural sunlight for 24 hours. After this time, the only difference noticed from the original samples was the presence of condensation in the top of the tube with titania-silica powder in it. This may indicate that photocatalytic oxidation occurred, since a product of PCO is water.



**Figure 29. Initial set-up of simple PCO experiment using methylene blue.**



**Figure 30. Resulting test tubes after 24 hours of exposure to visible light.**

The second test proved slightly more conclusive. Four aerogel samples (samples 2I, 2K, 2L, 2M 30%) were inserted into four test tubes with 10mL of 50 $\mu$ M aqueous methylene blue solution. These samples were placed in the solar simulator and exposed to 765 W/m<sup>2</sup> of simulated sunlight. The picture below shows the four samples after thirty minutes in the solar simulator. All samples were originally much bluer than seen below.



**Figure 31. Samples TiSi2I, TiSi2K, TiSi2L, TiSi2M 30% after 30 minutes in the solar simulator.**

Figure 32 shows absorbance of the original methylene blue solution with no titania-silica, before exposure in the solar simulator, with spectra of the four samples after exposure. Although the aerogel particles were in suspension and caused some scattering, it is evident that methylene blue was degraded in all samples due to the absence of peaks seen with the methylene blue sample.

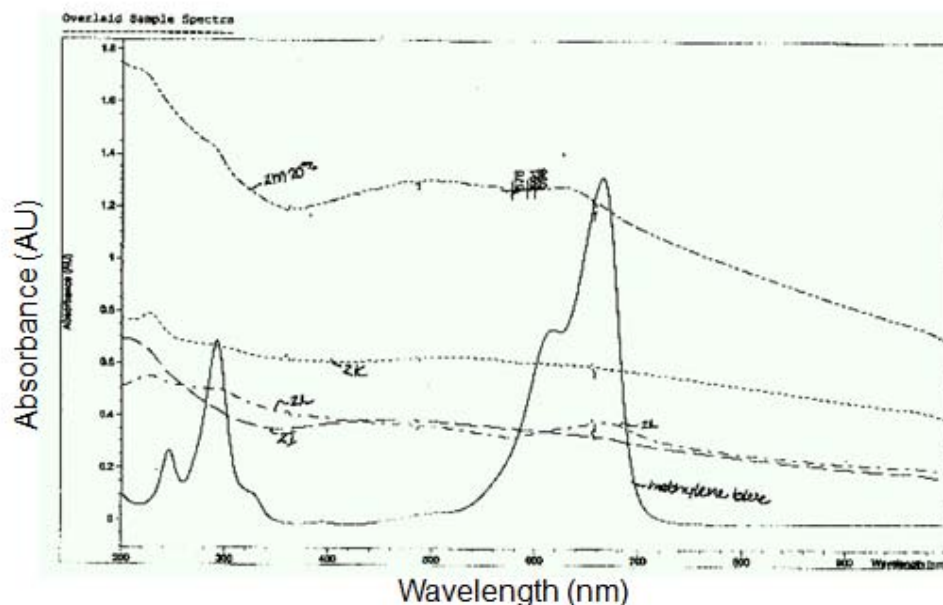


Figure 32. Spectra of titania-silica samples in methylene blue after exposure in the solar simulator.

For the third experiment, the same solar simulator conditions were used, but only TiSi2O- 30% Ti samples were tested. The first two samples were both covered throughout the entire experiment, one with only 50 $\mu$ M aqueous methylene blue solution (sample A), and the other with the methylene blue solution and 0.03g of aerogel sample (sample B). The third sample, sample C (pure methylene blue), was exposed. The last three samples had aqueous methylene blue solution with 0.03g, 0.015g, 0.008g of aerogel sample, for samples D, E, and F, respectively. Absorbance spectra were taken after 15 minute, 30 minute and 45 minute exposure in the solar simulator at 765 W/m<sup>2</sup>. Figure 33 shows the initial solution along with amounts of aerogel sample used for respective samples.



Figure 33. Aqueous methylene blue solution and aerogel samples to add to each test tube.



Figure 34. Test tubes in alphabetical order after 15 minutes of exposure in the solar simulator.



Figure 35. Test tubes in alphabetical order after 30 minutes of exposure in the solar simulator.





**Figure 36. Test tubes in alphabetical order after 45 minutes of exposure in the solar simulator.**

After 15 minutes in the solar simulator, there was noticeably less blue in samples D, E, and F and no visible change in sample C. There seemed to be even less blue after 30 minute exposure, and still no change in the color of sample C. After 45 minutes in the solar simulator, all methylene blue seemed to be entirely gone, and there seemed to be slightly less blue in sample C, which is likely due to bleaching. When samples A and B were uncovered, there seemed to be no change in color, which was confirmed by absorbance spectra. Figure 37 shows the spectra taken throughout the experiment. Methylene blue can be seen in the 650nm peak at the bottom. With the exception of sample B baseline and after 45 minute measurement, this peak is not seen the other samples, which is indicative that the methylene blue was degraded during the experiment.

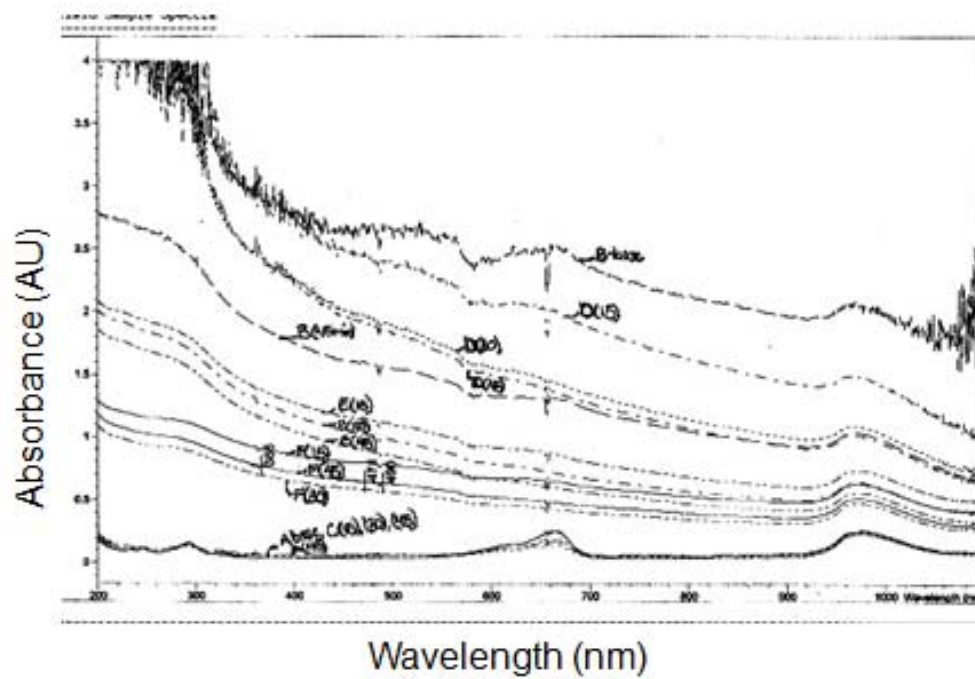


Figure 37. Spectra taken during the second solar simulator experiment. Each line is labeled with what sample and how long it was exposed.

## CHAPTER 4: PHOTOCATALYTIC OXIDATION OF TOLUENE

### Photocatalytic Oxidation Test Apparatus Design

A flow-type test apparatus was modeled after reactors found in the literature (Yoda 2000, Maira 2001). Air was chosen to be the primary gas, instead of oxygen or nitrogen, in order to duplicate ambient conditions. A rotameter was used to measure the flowrate, which was typically set to 311 mL/minute using a carboloy float (Sigma-Aldrich). An air bubbler was used to humidify the air (ChemGlass), but the addition of water vapor was not included during initial testing. Toluene was the VOC used to contaminate the airflow and would be added to the air stream using a magnetic stirbar in a flask, which was enough to vaporize the toluene liquid due to its high vapor pressure. Toluene was also one of the least harmful VOCs found in previous research. The toluene addition glassware used resembled an Erlenmeyer flask with a removable top which had inlet and outlet ports (see Figure 38 below).

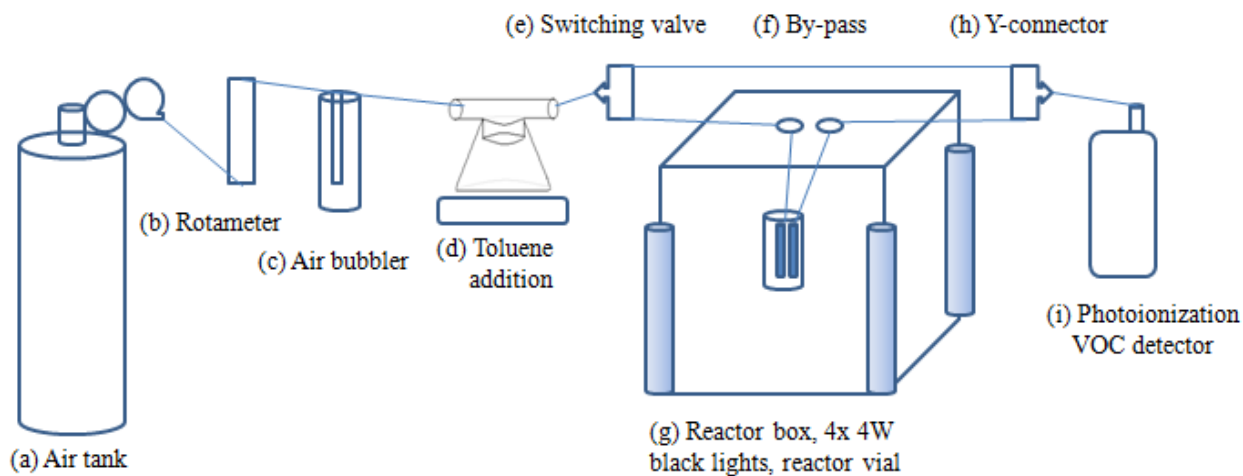


Figure 38. Schematic of the PCO test apparatus designed.

The switching valve was a three-way elliptical valve (Cole-Parmer) with appropriate adapters attached. This allowed the air stream to either (1) flow through the by-pass valve, without any contact with the catalyst or UV exposure or (2) flow through the reactor vial while being UV-illuminated. The reactor box used was built out of foam board and lined with aluminum foil to increase UV reflection. The UV light sources were four 4W blacklights (Blacklights USA) and notches were cut out of each corner of the reactor box for insertion of the light sources. The reactor vial (23mm OD x 110mm long, see Appendix B) was made from quartz and fabricated using a local glassblower. Quartz was chosen because it allows the passage of UV light. The reactor vial was sealed using a two-holed, size 3 rubber stopper (Sigma-Aldrich). The inlet and outlet of the reactor vial were initially Pasteur pipettes, however they kept breaking, so the local glassblower used in making the reactor vial donated thin quartz tubes (4 mm OD x 2 mm ID) of two lengths (200 mm and 100 mm) to be the inlet and outlet, respectively. The y-connector (Cole-Parmer) recombined both flow options and lead to the port where samples were placed into gas bags to be analyzed by the VOC photoionization detector (Photovac 2020 ComboPRO, details in Appendix C). The y-connector was later removed, due to suspected backflow through it. All of the parts in the system are connected with laboratory grade (R-3603) 1/4" ID tygon tubing. All part numbers and prices can be found in Appendix F. Initial tests used the Photovac 2020 ComboPRO (specifications found in Appendix C), however it was not designed to handle the humidity that was to be introduced to the system with the addition of water vapor, so a second VOC detector was used for the later tests. This was an Ion Science PhoCheck Tiger with data logging capabilities and specifications can be found in Appendix D.

## **Photocatalytic Oxidation Procedure & Results**

### *Preliminary Tests*

Preliminary testing was done to confirm various aspects of the system, before more controlled testing was performed. The first aspect of the system tested was the stability of toluene concentration flowing through the bypass, in order to determine the level of concentration before switching flow to run through the reactor.

About seven tests were performed using the Photovac, and about ten were performed using the Ion Science PhoCheck Tiger. The Tiger instrument was utilized to better handle humidity that was introduced into the system with the presence of water vapor. Additionally, only the most informative tests are presented in this and the following section. Other results can be found in the appendix.

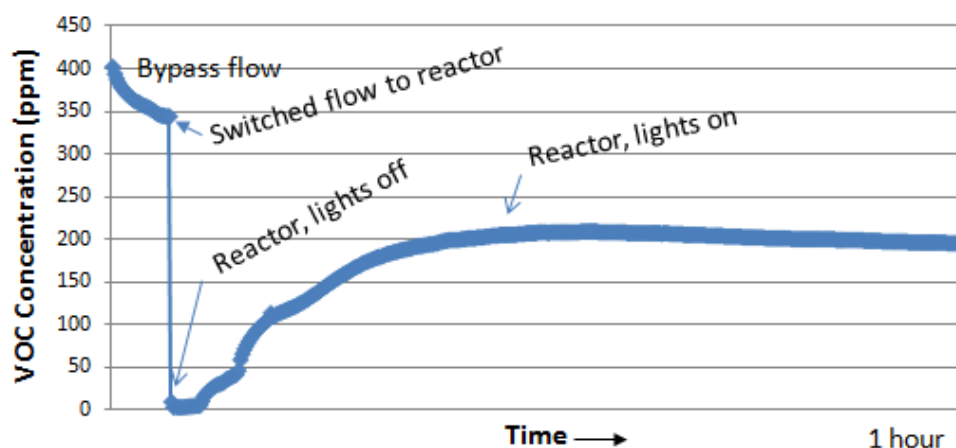
Initial testing was done to determine the stability of the system and whether or not gas bags should be used in testing. Although gas sampling bags were recommended by the Photovac manual, simply hooking the outlet tube to the instrument worked much better than any other option. The stirbar speed was also varied to see how sensitive the system was to the stirbar speed in the toluene addition glassware. It was found that the system is not very sensitive to changes in the stirbar speed. Preliminary testing also explored flow through bypass versus flow through the reactor, which produced quite different results, however, additional testing further explores these different flows.

### *Photocatalytic Oxidation Testing with PhotoVac*

Test four was conducted to determine whether or not a drop in concentration is achieved while running the airstream through the reactor with the UV lights off. The effluent VOC concentration with the lights off was suspected to be similar to the bypass

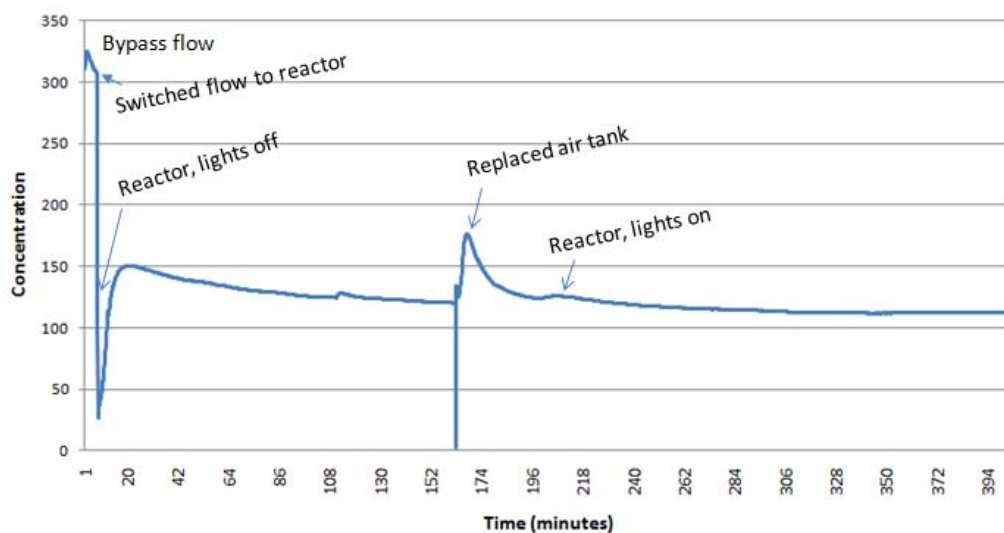
concentration. The same system conditions were present as previous tests; 60 mL of toluene, stir-plate speed of 125 rpm, flow rate of 311 mL/min, pressure of 25 psi. At the start of the test, air flowed through the bypass. The Photovac instrument was previously set to record data at 60 second intervals. This was changed to record data every 10 seconds. The bypass concentration was measured for five minutes before routing the flow through the reactor with the UV lights left off. This was left untouched for twenty minutes before turning the UV lights on. The lights were left to warm up for about twenty minutes and measured the flow thirty minutes beyond the warm-up period. Following this, the test was concluded.

At the initial part of test four, flow through the reactor proved to be at a similar concentration as previously seen and decreased with time. Once flow was routed through the reactor, the VOC concentration decreased significantly. This was an interesting result, as the UV lights were not turned on, so photocatalytic oxidation could not have been occurring. After about twenty minutes, the system seemed to reach steady state and the reactor lights were turned on. After an initial warm-up period, the concentration slowly decreased, specifically about 15 ppm over 30 minutes. This result indicates that photocatalytic oxidation may be occurring, it just may take a significantly longer amount of time than originally expected.



**Figure 39. Flow through reactor with and without UV illumination in Test #4.**

Test five repeated test four. The system conditions remained the same; 60 mL of toluene, stir-plate speed of 125 rpm, flow rate of 311 mL/min, pressure around 25 psi. The airstream first flowed through the bypass for about five minutes. The airstream was then routed through the reactor with the lights off until it seemed to reach a steady state. The UV blacklights were then turned on. In this case, before the blacklights were turned on, the air tank needed to be added to the system, and the old one removed. After forty minutes to re-stabilize the airflow, the UV blacklights were turned on. The system remained on for three more hours before being turned off. The results seen during test five agree with the results found in test four. With the exception of replacing the air tank, system conditions were also the same.



**Figure 40. Flow through reactor with and without UV illumination in Test #5.**

Additional testing using the PhotoVac tested whether the catalyst could be reactivated by flowing clean air through the reactor for a few hours. Another test was done to investigate flow through titania-silica aerogel powder with no glass beads present, as well as flow through an empty reactor vial. These details can be found in the additional PCO of toluene section of the appendix.

#### *PCO Testing with the PhoCheck Tiger*

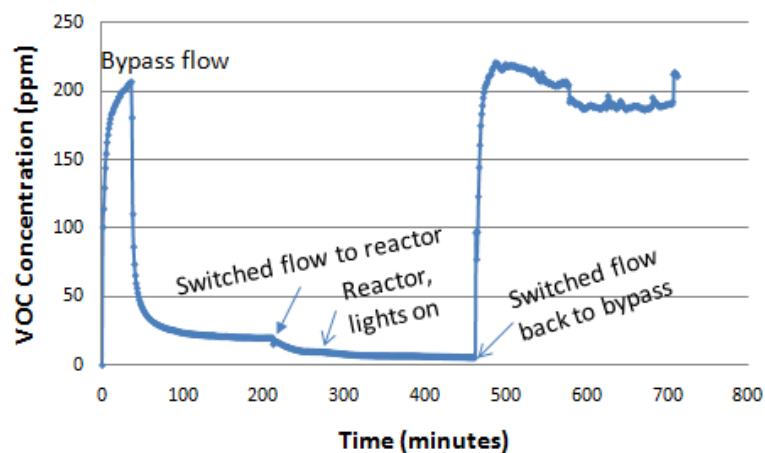
Following these initial tests, it was desired to add water vapor into the system. The PhotoVac was unable to handle high humidity levels, so another instrument was rented, the Ion Science PhoCheck Tiger, which was better able to handle the humidity that was to be introduced into the system. The PhoCheck Tiger was calibrated for isobutylene, so all presented concentration levels should be divided in half to get the true level of toluene present.



The first tests using the Tiger consisted of flowing contaminated air through the bypass and flowing through the reactor vial. It was hypothesized that the reactor vial had a cross-section that was too large to adequately supply enough light to aerogel material to efficiently perform PCO. Once this was realized, aerogel material was only placed in the small inlet tube in the reactor vial. For tests T6 and T7, there was also a good amount of aerogel material in the bottom of the reactor vial.

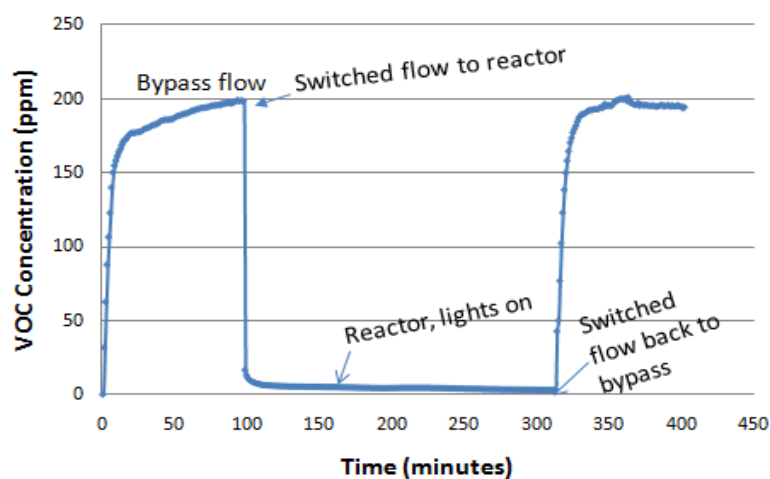
Test T6 was run with new aerogel material impregnated with glass beads from sample TiSi2U. The stirbar speed was set at 700 rpm, and flowrate at about 300mL/min, as usual. Since previous testing, the test set-up had been moved to a new lab and air tank was replaced by hooking up the system to the laboratory air. This air flow was not as steady as an air tank, but proved sufficient.

In Test T6 flow was routed through the bypass for the first four hours. The bypass concentration decreased inexplicably during this time. After approximately 200 minutes, the flow was switched to the reactor for about a half hour until the lights were turned on. A further decrease in concentration was seen, down to 6ppm. After a few hours, the batteries in the UV lights died, at which point the flow was re-routed to flow through the bypass again, and returned to about the original value of around 200 ppm.



**Figure 41. Test T6 measures flow through the bypass and reactor vial with aerogel material only present in the inlet tube and in the bottom of the reactor vial.**

Test T7 repeated test T6, since there was an odd drop in concentration during bypass flow. All other parameters remained the same. The drop in bypass concentration did not happen again.



**Figure 42. Test T7 repeated Test T6.**

### *Effects of Water Vapor*

Test T8 differed from tests T6 and T7 in that water vapor was introduced into the system. The water bubbler was filled with 20 mL of deionized water before the test began. The flowrate and stirbar speed remained the same as previous tests. The aerogel

material had not been replaced since the previous test to see if the water vapor would regenerate the catalyst sites.

After about an hour and a half of flow through bypass, the contaminated air was switched to the reactor. After this occurred, the concentration dropped to about 7 ppm. After a half hour of reactor flow, the UV lights were turned on for two hours. During this time the concentration dropped to 3 ppm. After this time, flow was switched back to the bypass where it increased back to previous levels. No quantifiable difference was seen with the presence of water vapor.

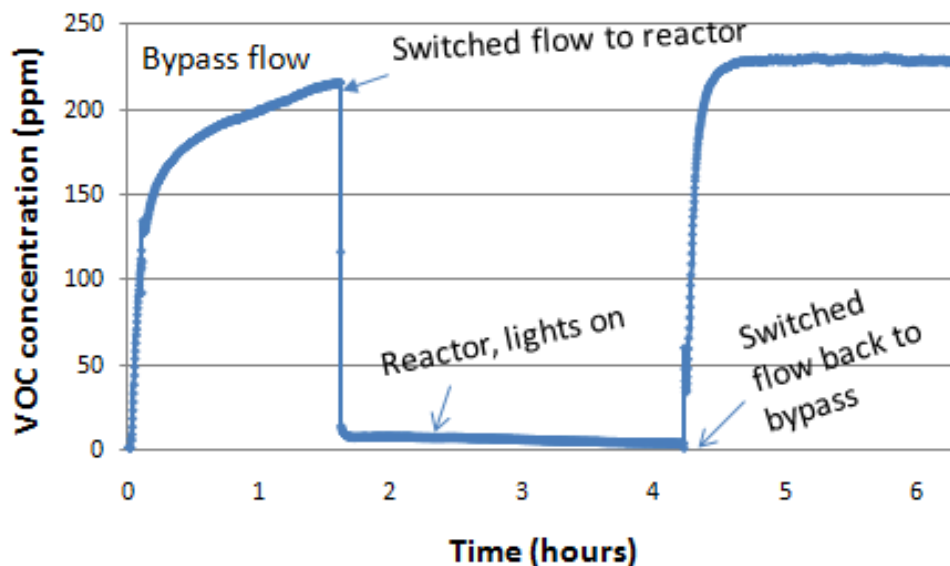


Figure 43. Test T8 introduced water vapor into the system.

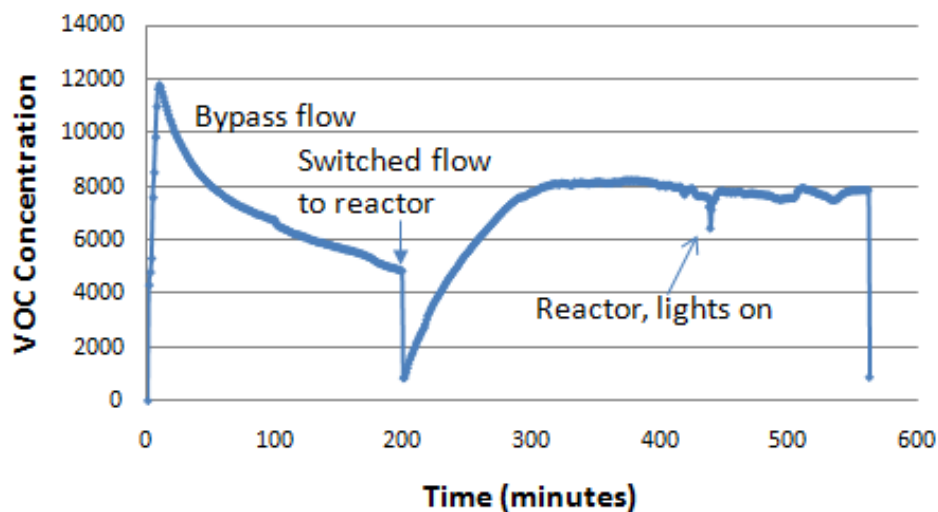
After test T8, most of the aerogel material was removed from the bottom of the reactor vial, leaving aerogel material only in the inlet tube. This was typically only about 0.5 grams of aerogel material.

### *Effects of High Levels of Toluene*

Another hypothesis was that the system needed to be saturated with toluene so that it would not adsorb any additional toluene into the tygon tubing. This was attempted during tests T10 and T12, however a stable amount of toluene in the bypass was not achieved, which may indicate that tygon tubing should not be used for this application.

In preparation for test T10, the water and toluene were switched in the system so that air bubbled through toluene and water vapor was added using a stirbar. An amount of 20 mL of toluene was in the bubbler and 60 mL of deionized water was present in the stirbar addition glassware, which were the same respective amounts of liquid previously present in each piece of glassware.

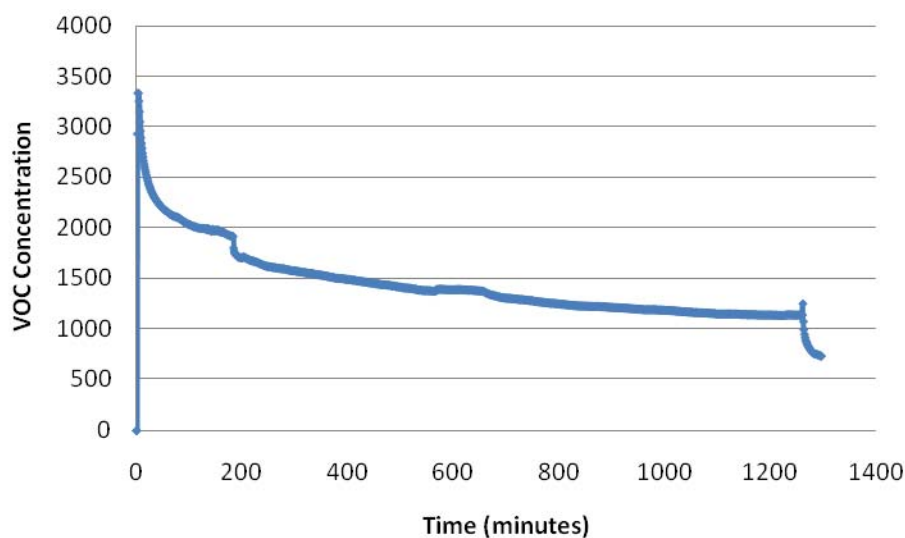
T10 bubbled air through toluene which then flowed through the bypass for about four hours and continued to decrease. The drop in concentration around 200 minutes occurred when the flow was routed through the reactor, which then showed an increase in concentration back to about 8000 ppm, which seemed to be about steady state. The small drop in concentration at about 450 minutes occurred when the UV lights were turned on, however the concentration quickly returned to about the same level as it previously was.



**Figure 44. Test T10 attempted to saturate the system with high levels of toluene flowing through the bypass and reactor vial.**

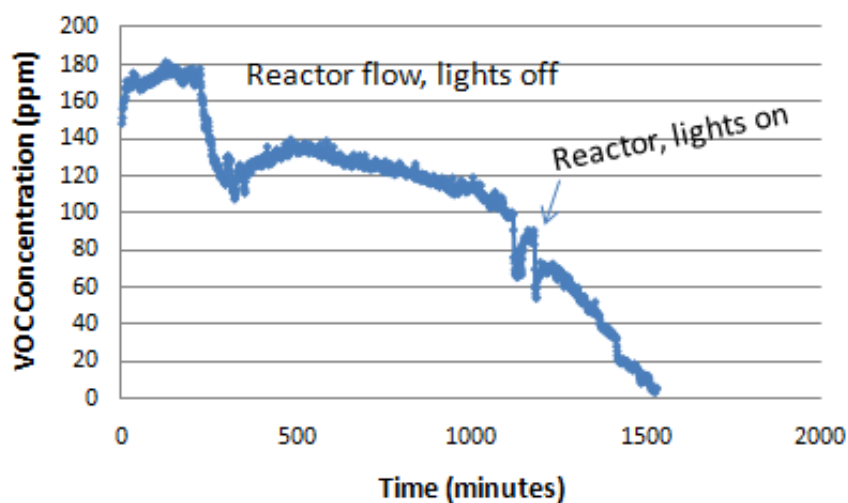
#### *Long Term PCO Testing*

Test 12 was the last test performed and by far the longest, as the system was running for about three days, whereas the previous tests had only been a matter of hours. Test T12 was also done at high levels of toluene, accomplished through bubbling air through toluene. Test 12a shows flow through the bypass, which showed a similar continual decrease that had been seen in Test 10. Towards the end of the plot the instrument was removed from the system and charged for a few hours before being replaced. A drop in VOC concentration was seen at approximately 1350 minutes. This drop in concentration may have occurred over the time that the instrument was charging, but was not documented until the instrument was replaced. Before the instrument was replaced, 60 mL of additional toluene was added to the bubbler.



**Figure 45. Test T12 saturated the system with high levels of toluene flowing through the bypass.**

Test 12b shows flow through the reactor. Toluene was periodically added throughout this time. Towards the end of the test, at approximately 1200 minutes, the UV lights were turned on. There is an obvious decrease in concentration after this occurred, from about 90 ppm down to 5ppm, which is likely to do photocatalytic oxidation occurring.



**Figure 46. Test T12 continued with flow through the reactor vial with and without UV illumination at high levels of toluene concentration.**

## CHAPTER 5: DISCUSSION

The recipe and process used to fabricate titania-silica aerogels was modified to make the best possible aerogels in the shortest amount of time. It was first noticed that mixing aerogels for five minutes after all of the precursor chemicals are combined, but before putting them into the hot press resulted in better aerogels, so five minutes became the standard mixing time at this point. It was also noticed that aerogel monoliths were not homogenous. The bottom parts seemed more silica-like, while there was frequently a top layer which resembled a titania aerogel. A hypothesized solution was to heat the precursor solution up faster, since previous research using a mold that allowed the user to view the hot press process showed that convection occurs mixing up the hot press solution during the second step of the RSCE process. Using this knowledge, a process using two times the previous heat rate ( $6^{\circ}/\text{min}$  as opposed to  $3^{\circ}/\text{min}$ ) was used to fabricate the batch TiSi2M. When the heat rate for step two was increased, the dwell time for step two was also increased so that the entire process would take the same amount of time as the original process. When this worked, a process with three times the original heat rate ( $9^{\circ}/\text{min}$  as opposed to  $3^{\circ}/\text{min}$ ) was used to fabricate TiSi2M. There continued to be nonhomogenous monoliths, so a process with three times the original heat rate, as well as double the catalyst was used to fabricate TiSi2O. This provided visibly homogenous monoliths. The recommended process is shown in Table 4, with a temperature rate of  $6^{\circ}/\text{minute}$  in Step 2, instead of  $3^{\circ}/\text{min}$ . This process results in bulk densities between  $0.027\text{-}0.035\text{ g/cm}^3$ , skeletal densities between  $2.39\text{-}2.94\text{ g/cm}^3$ , and BET surface areas between  $279\text{-}554\text{ m}^2/\text{g}$ .

Bulk density shown in Figure 5 shows that the first recipe produces far more dense monoliths than the second method. Skeletal density shows that samples that are more silica-like have lower skeletal density, and more titania-like have higher skeletal density. Surface area is higher with the first fabrication method. Samples that are more silica-like have higher surface area, and samples that are more titania-like have lower surface areas. When looking at the BJH pore distribution results, the broader peaks seem to be the samples that are more silica-like; while the two samples with the lowest pore volume have a higher level of titania. The similarities in FTIR spectra show that although samples look like they have more titania at the top of a monolith and more silica at the bottom, this may not be the case.

The preliminary photocatalytic oxidation research performed using methylene blue in an aqueous was promising. Many of the articles discussing previous research stated that anatase titania performed better than amorphous titania. The Brodzik recipe used had the lowest amount of anatase when compared to the other three recipes used. However, the XRD analysis showed that anatase titania was present, which was promising.

Figure 30 shows the result of the initial methylene blue experiment. Although there was not a visible change in the color of the solution, it was a very concentrated solution and there was very little sunlight during the period of observation. It was noted that in the tube with titania-silica sample, there was condensation in the top of the tube, and there was none in the methylene blue test tube. This may indicate photocatalytic oxidation occurred since one product of PCO is water.



The spectra taken after the first solar simulator experiment shows the baseline peaks of methylene blue. Although the suspended aerogel particles cause some scattering, the methylene blue peaks were no longer evident. The successive pictures at each 15 minute interval show a reduction in methylene blue. Figure 31 shows that methylene blue does not degrade when it is not exposed to light, or when titania-silica aerogel is not present. This confirms that the decrease in methylene blue was due to photocatalytic oxidation.

The photocatalytic test apparatus was designed to be operated at room temperature. Most of the parts were not meant to be used with toluene, but most of the background research done showed that it could work, if the system was not used above room temperature. An apparatus designed for the use of toluene as part of the working fluid would have stainless steel tubing, at least beyond the toluene addition point, as well as a different switching valve. Additionally, a more permanent apparatus would have a sturdier reactor box, and possibly brighter UV lights. The tygon tubing may have been the reason why the system could not be saturated, as well as why the bypass concentration did not stop decreasing during tests T10 and T12.

The results found during the initial tests of the PCO test apparatus are quite interesting. In general, they show that it is easier to test the effluent directly from the outlet tube, avoiding the use of gas bags, and that flowing through either aerogels or glass beads will decrease the concentration of any VOCs present, which should only be toluene. There is a small chance that the toluene is being partially broken down, but a byproduct, such as benzaldehyde, is being formed and registering as a VOC. Gas chromatography has the ability to identify such products, however, it is likely beyond the

scope of this project. Toluene is most likely being absorbed to either the titania-silica aerogels and/or the glass beads, since the VOC concentration decreases even when the UV lights are not turned on. The results shown in test #7b, seen in the appendix, show that flow through the reactor vial without any aerogel material or glass beads is comparable to flow through the bypass tubing.

Results were repeated enough to assume that the large drop in concentration after switching from bypass flow to reactor flow is due to adsorption of toluene by the aerogel material. Once the UV lights are turned on, a further decrease in concentration is seen, which is where photocatalytic oxidation is likely occurring. Test T8 showed a total decrease of 224 ppm, or a 98.3% decrease. Of that decrease, 98.4% occurred before the UV lights were turned on, and therefore can be attributed to adsorption. After the UV lights were turned on, the other 1.5% decrease occurred, which can be attributed to photocatalytic oxidation. The high toluene concentration case (test T12) had a decrease of 725.8ppm, which was a 99.4% decrease. Of this decrease, 91.2% of it occurred before the UV lights were turned on, which can be assumed to be adsorption into the aerogel. The other 8.8% of the decrease occurred after the UV lights were turned on and therefore can be assumed to be photocatalytic oxidation. Yamazaki-Nishida saw similar results with a trichloroethylene decrease from 460 ppm to 3 ppm, or a 99.3% decrease (1993).

Water vapor did not seem to have any effect on the system, however it was not confirmed that the aerogel material had adsorbed as much toluene it was able to. If this occurred, then it would be expected that the reactor concentration rise to the level of the bypass concentration, which never came close to happening.

The surface area of the aerogel material present in the later tests (about 0.5 grams) was compared to the surface area of the tygon tubing to make sure that the majority of adsorption was not due to the tubing. The magnitude of the surface area of aerogels was almost 100x that of the tubing. However it was suspected that at much higher levels of toluene, the tygon tubing may be a problem. The system seemed to be much more stable at lower levels of toluene, or when air was not bubbling through the toluene.

## CONCLUSION

In conclusion, titania-silica aerogels can be fabricated using the rapid supercritical extraction method. Altering the processing parameters alter the resulting characteristics. Methylene blue can be degraded in the presence of UV and visible light using photocatalytic oxidation. A modified flow-type photocatalytic oxidation test apparatus was designed, built, and initial tests were performed. Testing indicates that the presence of aerogel material decreases the amount of toluene in a polluted airflow. Most of the decrease is likely due to adsorption of the toluene by the aerogel material, though a portion of the decrease in concentration is likely due to photocatalytic oxidation. Further testing with an improved system should be done to confirm these results, and try to further increase the amount of photocatalytic oxidation occurring.

## FUTURE WORK

Future work should redesign the current system using something other than tygon tubing, ideally stainless steel or glass tubes. This will eliminate one variable in the testing. A different switching valve and different UV light sources should also be utilized. Further testing could be performed to determine how long it takes before the titania-silica catalyst is deactivated, whether or not it can be reactivated, and how water vapor affects this process.

Additionally, in the future, a similar test apparatus could be designed for implementation in any commercial and industrial building that uses recycled air, to improve the air quality by breaking down harmful VOCs.

## ACKNOWLEDGEMENTS

I would like to acknowledge Professor Ann Anderson and Professor Mary Carroll for all of their help and guidance throughout my various research projects. I would also like to thank the Aerogel Team for their constant support and alternative ideas. I would like to thank Professor MacManus-Spencer for her time and the use of her solar simulator. Professor Adrian was a great help in the design of my test apparatus. I would like to thank the Mechanical Engineering Department, especially Stan Gorski and Rhonda Becker, as well as the Mechanical Engineering Machine Shop for fabricating the molds used. The Chemistry Department and Chemistry Stockroom, particularly Kathy Ryan, were of great help as well. I would like to acknowledge the Internal Education Fund for funding, as well as the Presidential Green Grant, and National Science Foundation Grants ((NSF MRI CTS-0216153, NSF RUI CHE-0514527, NSF MRI CMMI-0722842, and NSF RUI CHE-0847901) that fund the Aerogel Lab at Union.

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## APPENDICES

Appendix A: Sample Characterization Sheet

Appendix B: Reactor Vial Drawing

Appendix C: Photovac 2020 ComboPRO details

Appendix D: Ion Science PhoCheck Tiger details

Appendix E: Additional PCO of toluene procedures & results

Appendix F: Spending Summary

Appendix G: IEF Proposal

Appendix H: Green Grant Proposal

## Appendix A. Sample Characterization Sheet

Characterization Sheet BATCH: \_\_\_\_\_ Operator Initials \_\_LB\_\_ BATCH

### Recipe 2

step 1	TEOS	4.5ml	4.2g	0.02 mole
	TIP	0.94ml	0.90g	0.0032 mole
step 3	EtOH	29.91ml	23.6g	0.512 mole
	H2O	0.97ml	1.45g	0.08 mole
	0.363M HCl	0.48ml	0.05g	0.00017 mole
step 5	water	0.24ml	0.24g	0.0128 mole
	EtOH	2.66ml	2.1g	
	NH3	0.42ml	0.38g	

Comments:

**Hot Press Process** Accudyne or **Tetrahedron** Program Number: \_5\_

Data File/Worksheet: \_\_\_\_\_

Start Time: \_5:45pm 3/22/10\_ End Time: \_\_\_\_\_

Step	Temp (°F)	Temp rate	Force (kips)	Force rate(kip/min)	Dwell time
1	90	200	15	600	6 hr, 30 sec
2	575	3	15	10	2 hour
3	575	200	1	1	15 min
4	90	5	1	600	30 sec
5	end				

Resulting aerogel:

PT trace:

Pictures of monolith:

BATCH

### Characterization

Density:

Mass \_\_\_\_\_ Diameter \_\_\_\_\_ Height \_\_\_\_\_

Picture & Excel table:

Density:

*BET surface area:* Sample file name \_\_\_\_\_

Empty test tube: Sample & tube: \_\_\_\_\_ Sample(before):

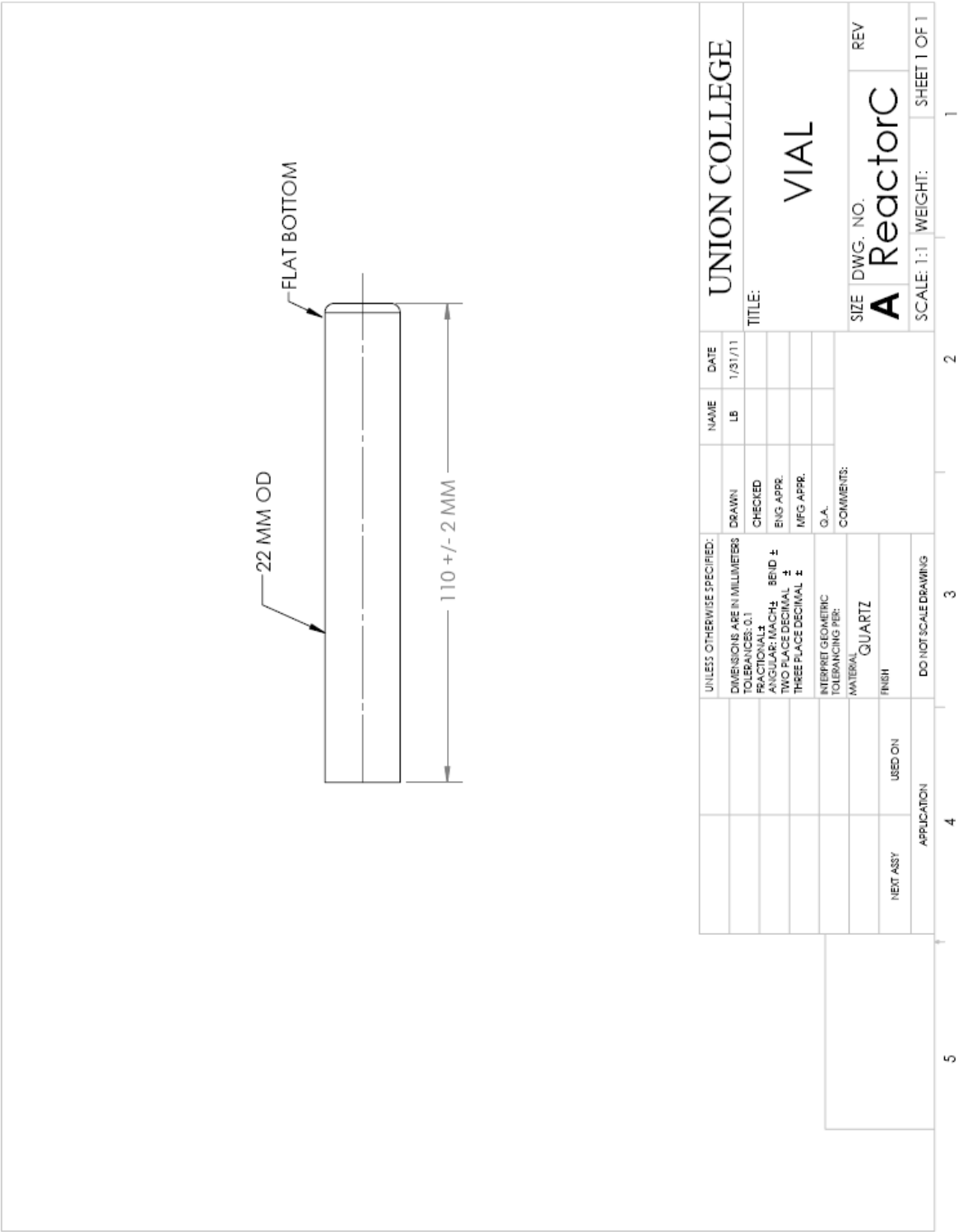
(After)Sample & tube: Sample :

Degas Port \_\_\_\_\_ TriStar Port \_\_\_\_\_

Results:



Appendix B. Reactor Vial Drawing





# 2020 ComboPRO™

## Portable Photoionization Monitor for VOC Measurement

- Combination Total **VOC** and **Benzene measurement**
- **Large, simultaneous** information display
- **Exceptionally simple** calibration and easy operation
- **Intrinsically safe** and rugged



## Applications

### ◦ Environmental

- Site characterization and remediation
- Leaking underground storage tanks
- Soil/water jar headspace screening

### ◦ Industrial Hygiene and Safety

- Workplace exposure assessments
- Indoor air quality studies
- Benzene exposure monitoring

### ◦ HazMat and Homeland Security

- Chemical incident response
- Personal protective equipment assessment
- Incident perimeter designation and maintenance

### Proven PID technology coupled with flexibility

The 2020ComboPRO represents the newest advancement in volatile organic compound (VOC) measurement coupled with operational simplicity. It is designed to respond quickly in emergency response situations while providing plenty of brainpower when you need it for comprehensive data analysis. With its proven photoionization (PID) technology and extended range of 0.1 ppm to 10,000 ppm, the 2020ComboPRO measures a wide variety of chemicals for environmental, industrial hygiene, and emergency response applications. Plus, with the quick connect pre-filter tube assembly, it can measure benzene... a critical compound to identify in many environmental and industrial hygiene monitoring activities.

### Easy operation

Designed with the field professional in mind, the 2020ComboPRO features a large graphic display that is easy to read, even with a full face respirator, and the large keypad buttons are easy to access even with heavy hazmat gloves. Simultaneous real-time measurements and maximum hold readings provide all the important information you need without switching modes. The 2020ComboPRO provides unsurpassed operational simplicity, and calibration is quick and easy. And, the ease of use doesn't stop there. Our ProComm software lets you download lots of data with the push of a button, offering datalogging and documentation capability.



## Applications



### Emergency Response and Hazmat

Hazmat and Emergency Response Teams require portable, reliable instruments to quickly characterize accidents, spills and contaminated sites. With its quick TVOC response time of less than 3 seconds, results are provided rapidly so immediate decisions can be made regarding the level of protective equipment required and the appropriate clean-up actions.

### Benzene Monitoring

Benzene is a recognized carcinogen and atmospheric pollutant. The 2020ComboPRO can specifically measure for benzene through the quick connect pre-filter tube developed for Photovac by Dräger Safety AG.

### Health and Safety Monitoring

The 2020ComboPRO is the instrument of choice for personal safety monitoring because it responds best to a wide variety of toxic VOC's. Audible and visual alarms for STEL, TWA and real-time Peak levels provide the health and safety professional with the right information to alert workers to potential health risks.

### Soil/Water Jar Headspace Screening

The 2020ComboPRO can detect a wide variety of VOC's from 0.1 ppm to 10,000 ppm, making it an excellent screening tool for VOC's in soil or water static headspace.

### Site Characterization and Remediation

The 2020ComboPRO is ideally suited for site screening to determine the extent of contamination present by providing the concentration and defining the perimeter, while monitoring for potentially hazardous conditions during remediation.



2020ComboPRO with pre-filter tube assembly attached

## Specifications

### 2020ComboPRO includes:

- Specified UV lamp
- AC Charger (115V or 220 VAC)
- 6.7 in (17 cm) Teflon sample probewith spring relief
- 10 membrane filters
- Adjustable wrist strap
- Multi-tool
- User reference card
- User manual (CD)

### 2020ComboPRO with field kit adds:

- Hard shell carrying case
- Spare 8 hour rechargeable battery
- Calibration gas regulator
- ProComm software
- Computer cable

### Optional Accessories

- 2020ComboPRO Benzene Pre-Filter Tube Holder
- Benzene Pre-Filters (pkg. 10)
- Calibration gas (isobutylene in 1ppm, 10 ppm or 100 ppm concentrations)

Specifications are subject to change without notice

### Detector

Photoionization 10.6 eV UV lamp standard, optional 11.7 eV or 10.0 eV UV lamps.

### Size

9" (228.6mm) long x 3" (76.2mm) deep x 4.25" (107.9mm) wide at display, tapering to 2.6" (66.6mm at handle).

### Weight

1.9 pounds (0.86 kg).

### Display

Large 2 3/8" (6.03cm) x 1 3/4" (4.45cm), 8-line, 128 x 64 graphic LCD. Backlight manually activated.

### Keypad

Two dedicated keys (ON/OFF and CAL) and three menu keys.

### Datalogger Memory

VOC mode: 15,000 readings stored in instrument.

Benzene mode: 200 hours at 1 minute interval sampling.

### Response Time

VOC mode: Less than 3 seconds, to 90%. Benzene mode: Less than 60 seconds to 100%.

### Serial Output

RS-232, 9600 Baud, 8 bits, no parity for connection to Windows-based PC.

### Languages

English is standard. One of the following can be added as an option: Spanish, German, French, Italian.

### Operating Concentration Range

VOC Mode: 0.1 ppm to 100 ppm and 100 ppm to 10,000 ppm (isobutylene equivalent). Benzene mode: 0.1 ppm to 40 ppm (isobutylene equivalent).

### Operating Temperature Range

Operating temperature: 0°C to 50°C (32°F to 122°F) VS Certified temperature: 0°C to 40°C (32°F to 104°F).

### Operating Humidity Range

0 to 95% relative humidity (non-condensing). With optional humidity pre-filter tube in VOC mode: 0 to 100%.

### Battery Capacity

8 hours.

### Audio Alarm

85 decibels.

### Intrinsic Safety

Class 1, Division 1, Groups A, B, C & D. ATEX II 2 G EEx ib IIC T4 (TA = 0°C to +40°C).

### FCC

Class B digital device, pursuant to Subpart B, Class B of Part 15 of the FCC rules.



For further information on Photovac products, or to arrange a product demonstration, please contact a Photovac representative near you or email us at: [customerservice@photovac.com](mailto:customerservice@photovac.com) or contact Photovac, Inc.  
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REV. 01 02 08

*Appendix D. Ion Science PhoCheck Tiger Details*



## PHOCHECK TIGER

**World's Most  
Advanced PID  
Now Even  
Better!**

Independently  
verified as best  
performing PID  
technology



The PhoCheck Tiger hand held VOC detector with revolutionary PID technology provides the best available detection and software features, all ready to use straight out of the box!

### Key Features:

- Patented Fence Electrode Technology
- Dynamic range ppb to 20,000 ppm for specific volatiles
- Easy change miniPID Detector, Electrode Stack and Lamps
- Exceptionally easy to use and intuitive
- No complex set up procedures required via a PC
- Batteries certified to be changed within hazardous areas
- Fully upgradeable with selectable functions
- Choice of data logging options
- Battery life up to 30 hours
- Intrinsically Safe ATEX, IECEx and CUL approvals
- Rugged design with protective, removable rubber boot
- Loud audible sounders 95 dBA
- Bright LED and vibration alarms
- Wireless options
- Lowest running costs on the market
- 5 year instrument warranty

Advanced Gas Sensing Technologies  
**[www.ionscience.com](http://www.ionscience.com)**

**PhoCheck TIGER**

**Handheld VOC Detector**



PhoCheck Tiger with miniPID technology is the most advanced handheld photoionisation detector (PID) on the market for volatile organic compounds (VOCs). Choose from our full featured base unit, or upgrade your instrument with a number of optional functions.

**Best Proven PID Performance.** Ion Science patented Fence Electrode Technology is independently verified as the best performing PID for fast response and accurate readings, whilst effectively minimising humidity and contamination effects. The instrument's exceptional operation in high humidity environments is achieved without impairing other performance features.

**Dynamic Detection Range of 1 ppb to 20,000 ppm (gas dependant)** offering the widest detection range available. Detect VOCs down to ultra low ppb toxic thresholds levels up to 20,000 ppm. Readings can be displayed as mg/m<sup>3</sup> or ppm.

**Ready to Use Right Out of the Box** with no complicated programming and set up procedures via a PC to perform basic functions.

**Unique 6 Pin miniPID Detector Cell** with anti-contamination design dramatically extends run time. The easy change low cost filter, lamps and electrode stack can be replaced in seconds.



**Long Life, Field Replaceable Li-Ion Batteries** with up to 30 hours of use between charges. Batteries can be replaced safely, even in hazardous environments. Fast battery charging allows the instrument to be fully charged in six hours. 8 hours of use can be achieved from 1.5 hours charge. Dry cell battery options also available.

**Rapid Response in Less Than Two Seconds** - the fastest on the market - and as quick to clear down!

**Response Factors for Over 450 Gases.** The instrument is pre programmed with over 450 gas factors.

**Fastest USB Communication on the Market.** Directly connects to a PC via USB.

**Selectable Audible, Visual and Vibrating Alarms.** The instrument has two sounders reaching 95 dBA, two bright flashing LEDs and a vibration alarm for clear indication of gases present. Each function can be selected, switched off or volume turned down as required.

**Dedicated Flow Fail Sensor.** The instrument's separate flow sensor triggers an alarm when the flow drops below 100 cc/min for added safety.

**Intrinsically Safe** to European, Canadian and US approvals for safe use in flammable areas.

**Simple, One Handed Operation.** The PhoCheck Tiger is light, well balanced, comfortable to hold and comes with a convenient wrist strap as standard.

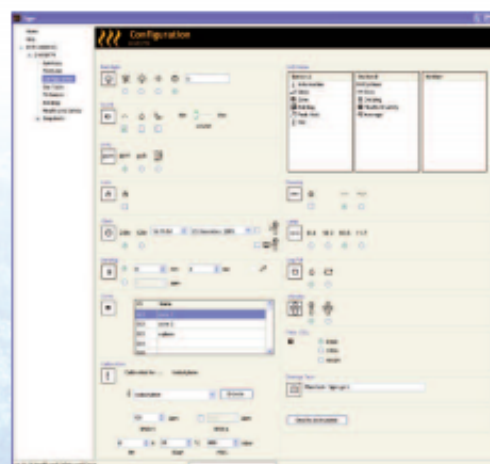
**Easy Key Pad Operation** and icon driven menu for ease of use across global markets. The soft keys are large enough to be easily operated, even when wearing the thickest gloves.

**Large, Clear Back-lit Display** allows for easy viewing in any light condition.



**Integrated Torch** for directing the probe in to dimly lit areas.

**Intuitive PC Tiger Software** **Supplied on USB Drive.** For users who wish to customise the instrument and download data; settings can be configured for one or multiple units, via one screen.



**Lowest Running Costs on the Market.** Inexpensive disposable parts, lamps and filters.

**Five Year Instrument Warranty.** Full warranty against workmanship, design, all electronics and hardware. Moving parts, filters and lamps excluded.

**Tel: +44 (0) 1763 208 503 • Email: [info@ionscience.com](mailto:info@ionscience.com) • Web: [www.ionscience.com](http://www.ionscience.com)**

## Kit and Accessories



Ion Science provides a range of PhoCheck Tiger kits to suit your requirements, along with an exclusive range of accessories. Further details can be found below. For more information and prices contact Ion Science or your local Distributor.

### PhoCheck Tiger Kit (part no. PTXSL8ME-0000) Contains:

- PhoCheck Tiger
- Rechargeable Battery (Li-ion)
- Battery Charger and Mains Adaptor
- Rubber Boot
- Explorer Case
- USB Memory Stick
- Zero Filter Assembly
- PTFE Filter Disc (dust filter)
- Removal Tool miniPID Stack
- Probe Tube (60mm)
- Sample Cleaning Compound Assembly
- Cleaning buds
- Lanyard (wrist strap)
- USB Cable
- Instrument Manual

### Instrument Accessories Include:

- Rechargeable Battery (Li-ion)
- Alkaline Battery
- 2.1mm DC jack - Cigar Lighter Plug Car Charger Lead
- Leather Instrument Holster
- Leather Instrument Harness
- Drager Tube Holder for Selective Detection of Benzene
- Flexible Probe Assembly
- 5m & 10m Extension Hose
- 9.8eV, 10.6eV and 11.7eV PID lamps

Note: PhoCheck is a US registered trademark, no. 2582554, and UK registered trademark, no. 2229452. Penza Electrode Technology is produced by Ion Science Ltd, and protected by U.S. Patent No. 7,048,032, EP 2474681, other patents pending.

## TECHNICAL SPECIFICATION

### MINIMUM RESOLUTION\*

1 ppb or 0.001 mg/m<sup>3</sup>

### MAXIMUM READING\*\*

20,000 ppm or 20,000 mg/m<sup>3</sup>

### ACCURACY\*

± 5% display reading ± one digit

### LINEARITY\*

± 5% to 100 ppm

### INTRINSICALLY SAFE APPROVALS

ATEX (II 2G Ex ia IIC T4 -15 °C ≤ Ta ≤ +60 °C), IECEx and CUL

### BATTERY LIFE

Li-ion: life up to 50 hours, charge time 8.5 hours

Alkaline: 3 x AA, typically 15 hours life

### LAMPS

10.6 eV Krypton PID lamp (standard) 9.8eV and 11.7eV lamps available

### DATA LOGGING\*

> 120,000 data log points including date and time stamp (33 hours at 1 log per second)

### COMMUNICATION

USB 1.1

### CALIBRATION

Via calibration kit accessory

### ALARM

Flashing LED and 85 dBA at 300mm (12") audible sounder

Selectable vibrating alarm

Pre-programmed TWA and STEL\*

Pre-programmed with 450 gases\*

### FLOW RATE

220 ml/min with flow fail alarm

### TEMPERATURE

Operating: -20 to 60 °C, -4 to 140 °F (non Intrinsically Safe)

Humidity: 0-99% RH (non condensing)

### PROTECTION

Designed to IP65 (heavy rain)

C  $\leq$  1180

EMC tested to EN61326-1:2006, EN50270:2006 & CFR 47:2006 Class A

### WEIGHT & DIMENSIONS

Instrument without probe

Width: 940 x Height: 90 x Depth: 60 mm (13.4 x 3.5 x 2.4")

Standard case

420 x 320 x 97 mm (16.5 x 12.5 x 3.8")

Instrument weight 0.72 kg (25 oz)

Packed weight: 5 kg (11lb oz)

All specifications are against isobutylene calibration at 25 °C, 50% RH and up to 3000 ppm unless otherwise stated. \*Model and gas dependent. \*\*Maximum reading is achieved with certain analytes such as ethanol.

\*For example: TWA 1. This publication is not intended to constitute a contract and specific details are changed without notice.

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## ***Appendix E. Additional PCO Procedures & Results***

### **Additional PCO of toluene procedures**

The initial amount of toluene placed in the toluene addition glassware was 60 mL measured out of a beaker. The speed of the stir-plate was set at 700 rpm. Tests were initially done using a gas bag, but then done holding the outlet tubing in front of the VOC photoionization detector. The speed of the stir-plate was changed during the duration of the test.

Test number two focused on gas bags, testing the concentration in the bypass twice and then switching to reactor flow, once the blacklights had been warmed up for fifteen minutes., and then one more test of the bypass effluent. Since the cost of each gas bag was relatively high and there was only access to a small number, one gas bag was used for the entire test, which was not ideal. There was 60 mL of toluene with access to the system, as was the case in test one, however, the stir-plate speed was increased to 1100 rpm.

Each of the gas bag samples taken from the bypass outlet filled the gas bags in roughly thirty seconds, which translates to a flowrate of roughly 2 L/min, which was much higher than the intended flowrate of 300 mL/min. However, when the flow was routed through the reactor, the gas bag took about five minutes to fill, and had a much higher concentration than any of the bypass samples. It is possible that this was due to backflow into the reactor via the y-connector when air was flowing through the bypass. It was also evident that flow through the reactor differed greatly than flow through the bypass and should be studied in greater depth.

Another observation was that the top of the toluene addition glassware “popped up” a noticeable amount when the flow pattern was switched from bypass flow to reactor flow. One change made was to remove the glassware containing the toluene from the system when the system is not in use. The system may have been absorbing toluene when the system was not in use, and removal prevents additional toluene absorbance from happening.

Test three was run with 60 mL of toluene present in the system, the stir-plate set to a speed of 700 rpm, and an air pressure of 25 psi. The pressure was likely the same in previous tests, but was not previously noted. The rotameter was adjusted to read a value of 120 which corresponds to a flow rate of 311 mL/min for the carboloy float that was placed in the rotameter. A reading was taken of the effluent concentration when the stir-plate was not turned on, so presumably no toluene was being added into the system. The stir-plate was then turned on and set to a speed of 700 rpm. To determine whether there is a correlation with stir-plate speed and effluent concentration, the stir-plate speed was turned down to 125 rpm. After about ten minutes, the valve on the rotameter was opened up completely and the stir-plate speed was turned up to 700 rpm to simulate previous testing conditions and to determine whether a similar concentration would be obtained test after test.

The second part of test three, tested flow through the bypass compared with flow through the reactor. The effluent concentration from the bypass was measured while the system flow rate was 311 mL/min and the stir-plate was set to a speed of 125 rpm. After about five minutes, the flow was switched to the reactor. The UV blacklights had been warming up for about twenty minutes by this point. After a few minutes, the flow was



routed back through the bypass to determine the VOC concentration of the airstream once more.

The purpose of test six was to reactivate the catalyst by flowing air without toluene through the reactor for a period of a few hours. The top of the toluene addition glassware was covered in parafilm so that outside air would not be drawn into the system. A flow rate of 150 mL/min was used, pressure was set to be 25 psi, and the airstream was routed through the reactor for the entirety of the test.

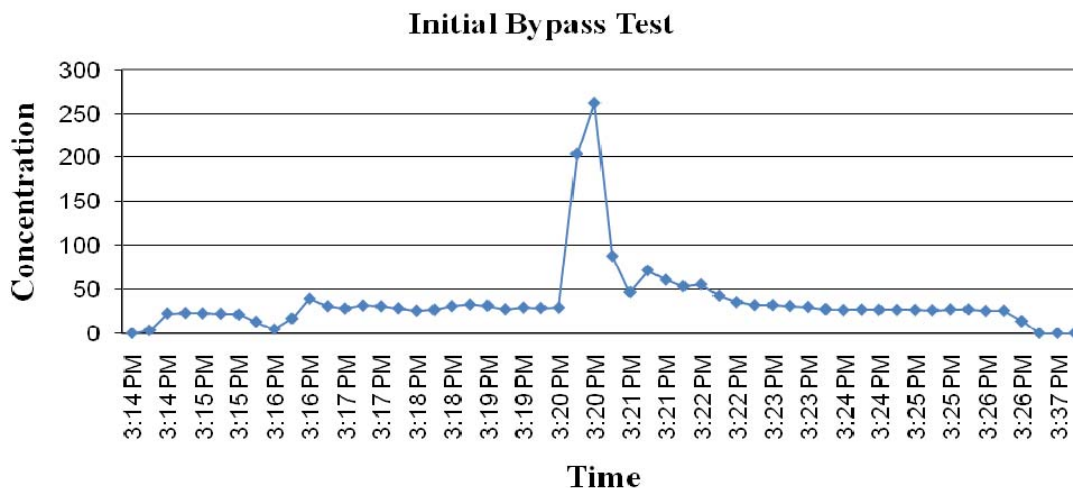
Before the first part of test seven began (#7a), the titania-silica aerogel material impregnated with glass beads was removed from the reactor vial and replaced with only titania-silica aerogel material. A thin layer of glass beads was added on top of the aerogel powder and monoliths to make sure that it does not flow into the system through the outlet. Once the reactor vial was placed back into the reactor box, the system was turned on. The system conditions remained the same as previously stated. The airstream was first routed through the bypass for about twenty minutes before switching to the reactor for about twenty minutes. The UV lights remained off. Following this, the flow was switched back to exiting through the bypass for another twenty minutes.

A second glass vial was set-up to mirror the reactor vial, but be placed in the bypass flow and not contain any aerogel material. The system conditions remained the same as previous tests. After about fifteen minutes flowing through the bypass vial with glass beads, it was disconnected and flow through the bypass tubing (as was done previously) was measured. After about ten minutes, the bypass vial was replaced, however the glass beads had been removed. The VOC concentration was then measured

for another five minutes. The last five minutes of testing flowed air through the reactor vial with only aerogel powder present, no glass beads.

### Additional PCO of toluene results

The initial test, testing the stability of toluene concentration through the bypass, proved to be reasonably stable, to within  $\pm 3$  ppm, which is within the uncertainty of the instrument. It also showed that gas bags are not ideal ways to collect samples, but work if entirely necessary. There also seemed to be a discrepancy between the concentration measured by the gas bag and the concentration measured by the outlet tubing. The first small peak is a sample from a gas bag. From 3:16 until 3:20, and from 3:22 until 3:26, the stir-plate speed was set to 700 rpm. Between 3:20 and 3:22, the stir-plate speed was increased to 1100 rpm, shown in Figure 47.



**Figure 47. Initial bypass test results.**

Test one was mostly used to get used to testing the effluent concentration and used both gas bags and held the outlet tubing up to the Photovac photoionization detector

inlet. The first readings tested the air in the hood where the test apparatus is set up and out of the air tank and were both zero. Both of the smaller peaks around 12:24 and 12:47 are analyses of gas bag samples. They are at comparable levels to the bypass outlet tested from 12:35 to 12:45. The small peak at 12:51 is also a gas bag sample. From 12:55 on are the results from the outlet. At 12:59, the flow was rerouted from the bypass to the reactor. The decrease in concentration at this point is encouraging. At 1:07, flow is changed back to flow through the bypass.

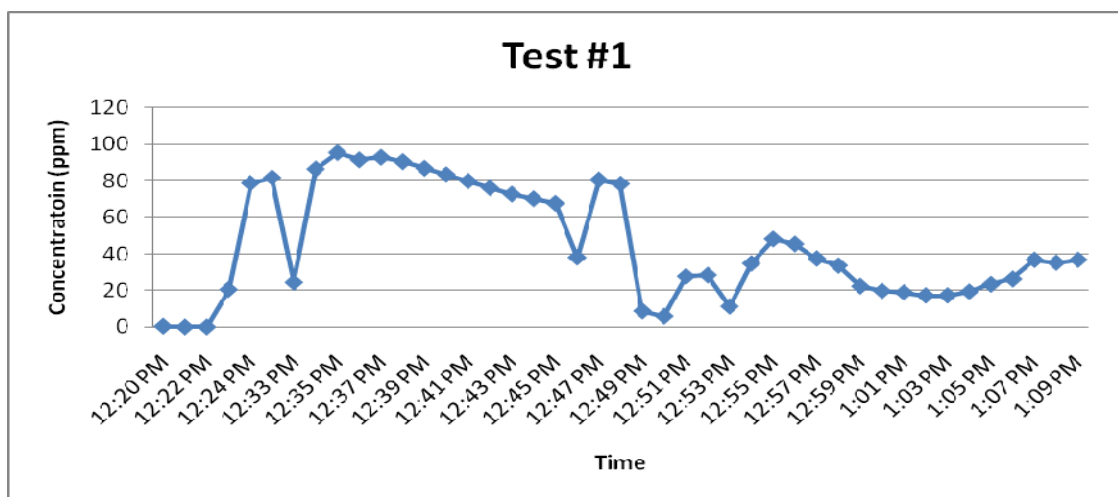
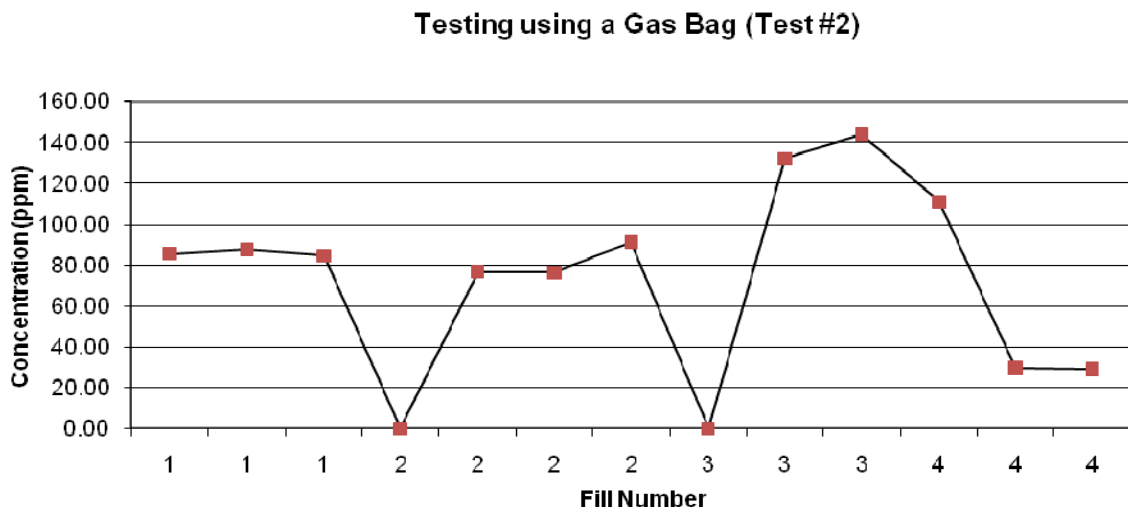


Figure 48. Test #1 results testing gas bags vs.outlet tubing analysis.

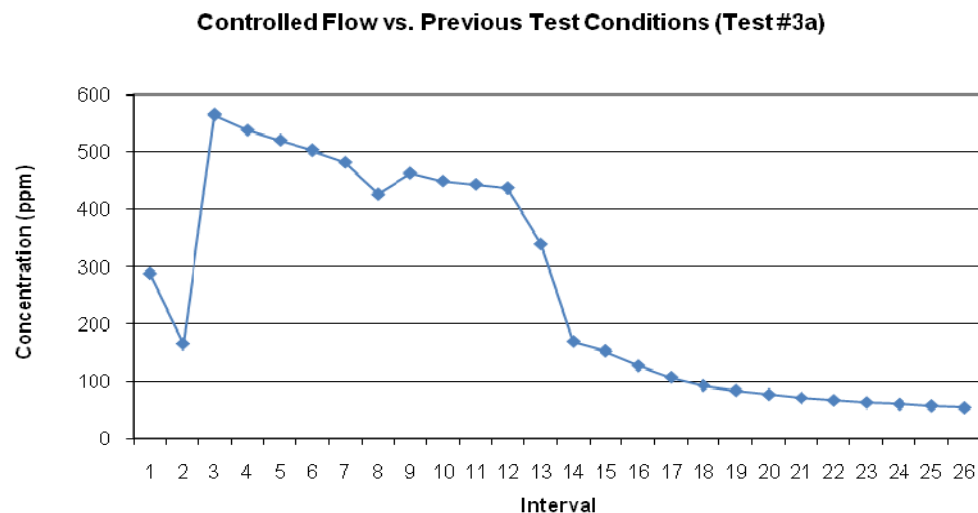
Test two was performed to evaluate the ease and accuracy of gas bags. A gas bag was filled four times, three times using flow through the bypass and once through the reactor. Flow through the reactor was fill number three, shown in Figure 24.



**Figure 49. Testing the VOC concentration using gas bags in Test #2.**

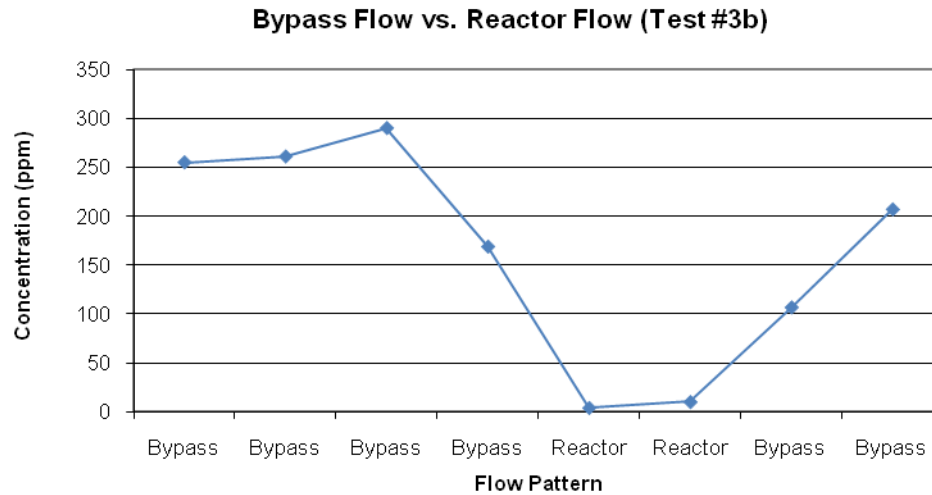
The first part of test three was performed to determine differences in conditions, such as flow rate and stir-plate speed. Initially, the flow rate was set to a known value of 311 mL/min, while adding toluene with a stir-plate speed of 700 rpm and is shown around interval three. After a short time, the stir-plate speed is changed to 125 rpm, and there was no noticeable change in concentration indicating that there may not be a clear correlation between stir-plate speed and toluene concentration.

Around interval 12, the rotameter valve was completely opened and the stir-plate speed was increased back to 700 rpm, to simulate previous testing conditions. At this time, the concentration decreased back to a level that coincides with previous test results.



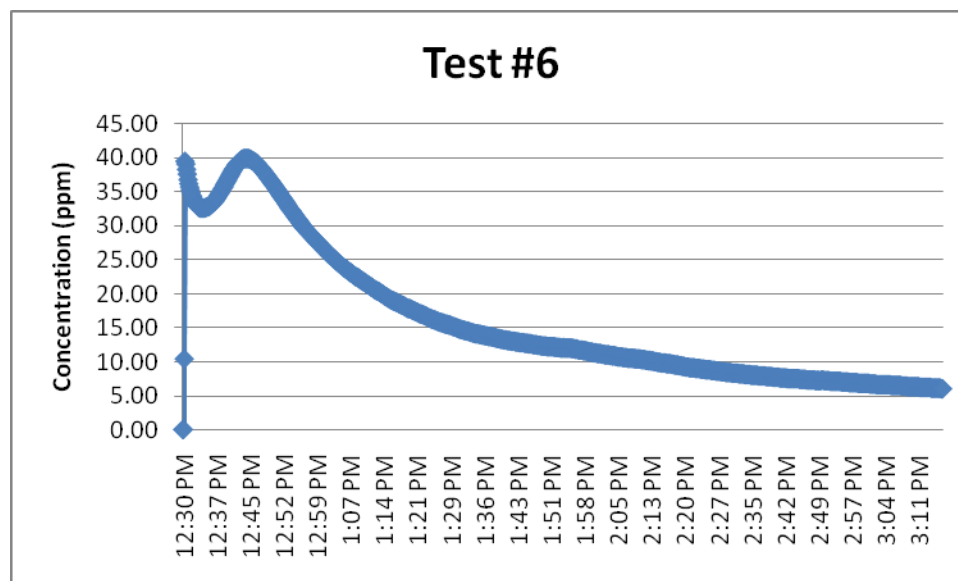
**Figure 50. Controlled flow vs. previous test conditions in Test #3a.**

The second part of test three, shown below, tested flow through the bypass compared with flow through the reactor. The VOC concentration was increasing slightly while flowing through the bypass. After the flow was routed through the reactor, the concentration significantly decreased from about 290 ppm to about 10 ppm. After this was maintained for a few minutes, flow was routed back through the bypass, and slowly returned to a VOC concentration exceeding 200 ppm. With time, this is likely to have increased back to the original levels. This seemed to be quite promising, but more testing was performed to make sure it was indeed a positive result.



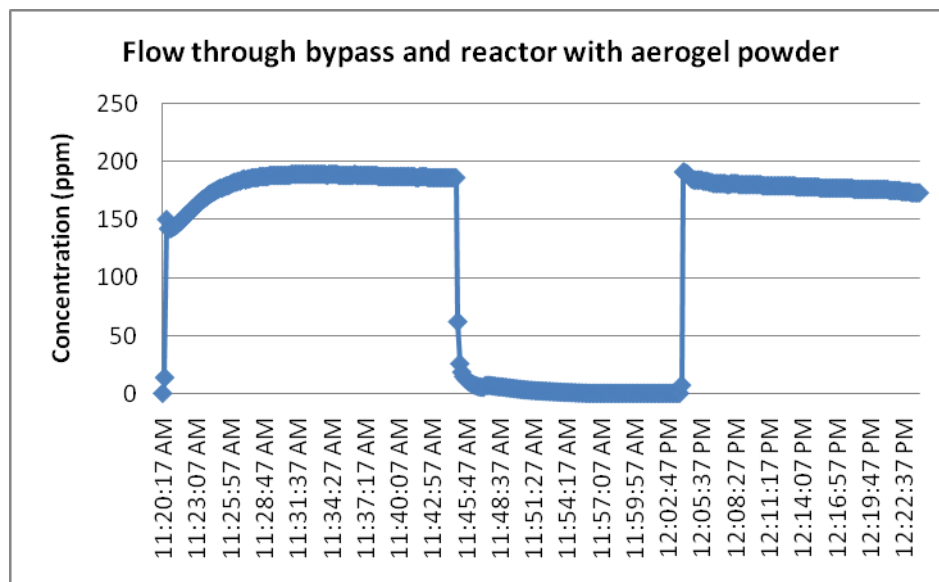
**Figure 51. Bypass flow vs. reactor flow in Test #3b.**

Test six was performed in an effort to reactivate the catalyst by flowing air through the reactor for almost three hours. In this time, the VOC concentration in the effluent air decreased from about 40 ppm to 6 ppm. This may have to be done periodically to clear out the toluene absorbed in the aerogel, particularly if photocatalytic oxidation does not completely breakdown the pollutant.



**Figure 52. VOC concentration at the outlet while flowing air over the aerogel catalyst in Test #6.**

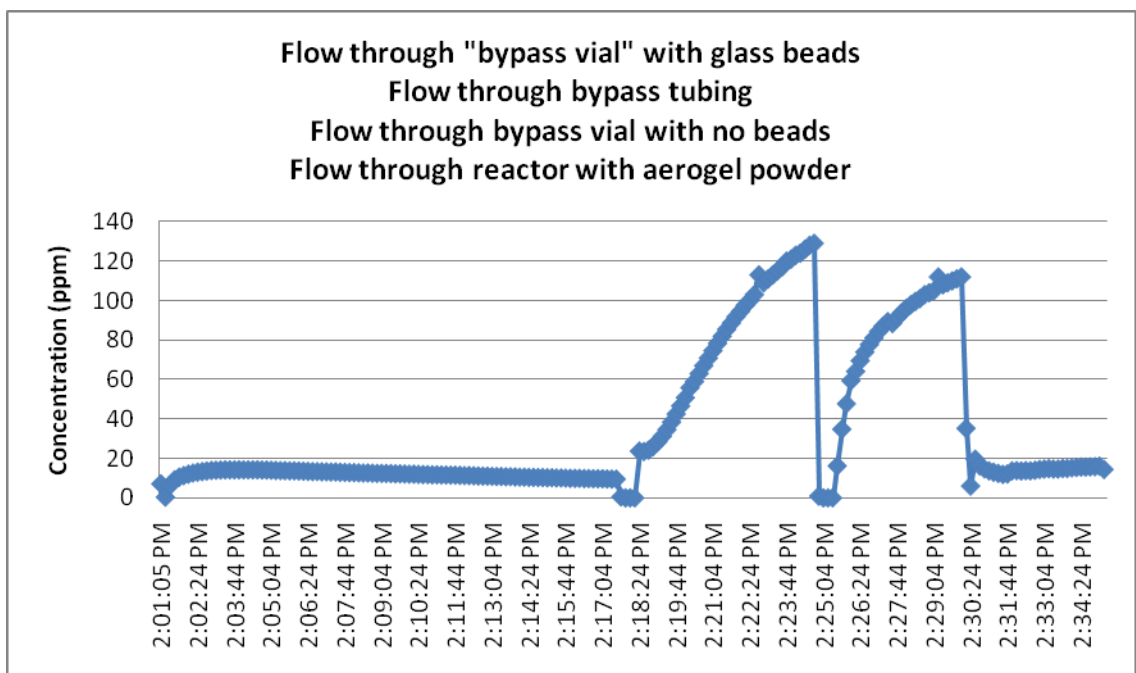
The first part of test seven was done to test whether flow was better through aerogel powder, replacing the aerogel powder impregnated with glass beads. Flow through the bypass was at a slightly lower level than seen previously, which is likely due to test six. After about twenty minutes when flow is routed through the reactor (with the lights off) the VOC concentration decreases to about 5 ppm. After fifteen minutes, the VOC concentration went down to 0 ppm, so the flow was routed back to flow through the bypass where it quickly returned to the previous level, at about 180 ppm.



**Figure 53. Flow through bypass and reactor with aerogel powder in Test #7a.**

The second part of test seven tested multiple different conditions to further evaluate possible reasons why flow decreases so much through the reactor. The first situation was flow through a bypass vial filled with glass beads. The VOC concentration was measured to be less than 20 ppm and slowly decreased over twenty minutes. The second situation was flow through the bypass tubing, which is typically what is measured in the bypass. This slowly increased but after about eight minutes, reached a level that

coincides with previous bypass output concentrations at about 125 ppm. The third situation was flow through the bypass vial without any glass beads. This showed a slow increase from 0 ppm, but almost matched the previously measured bypass concentration after about five minutes. Given additional time, it is likely that this would have increased to match the bypass concentration. The last situation that was measured was flow through the reactor with aerogel powder present, which was previously tested in the first part of test seven. Results showed a VOC concentration of about 15 ppm. It was previously measured to be between five and zero parts per million.



**Figure 54. Results of various test conditions performed during Test #7b.**



### Appendix F. Spending Summary

Date ordered	Company Name	Product Name	Product #	Price Each	Quantity	Total
		Glass beads, 0.5mm		25.70	1	25.7
2/3/11	GE glassblowing	Custom Glass Vial	n/a	12.50	2	25
2/4/11	Sigma Aldrich	Rotameter	23326	190.00	1	190
2/4/11	Blacklight USA	Fluorescent blacklight	n/a	9.95	4	39.8
2/4/11	Chemglass	Bubbler, adjustable	AF-0513-A-21	31.16	1	31.2
2/7/11	Walmart	Foam Board	n/a	3.94	2	7.88
2/7/11	Walmart	Aluminum Foil	n/a	2.84	1	2.84
2/7/11	Walmart	AA Batteries	n/a	5.97	2	11.9
2/8/11	Sigma Aldrich	Connector to male NPT	22085-U	15.10	1	15.1
2/8/11	Sigma Aldrich	Twistit 4-in-1 rubber stoppers	Z164321-50EA	23.60	1	23.6
2/8/11	Sigma Aldrich	Toluene, anhydrous 99.8%	244511-1L	43.80	2	87.6
2/14/11	Cole-Parmer	Elliptical valve, 3way, 4position	R-06472-17	72.80	1	72.8
2/14/11	Cole-Parmer	Barbed fitting NPT male pipe adapter	EW-30704-09	26.50	1	26.5
2/14/11	Cole-Parmer	Y-connector, PVDF, 1/4"	EW-30726-65	40.00	1	40
3/21/11	TRS-Environmental	PhotoVac 220 ComboPRO		\$185/week	1	185
6/2/11	TRS-Environmental	Ion Science PhoCheck Tiger-DL		\$21/day	42	900
					Total	1685
As of 6/3/11						

## ***Appendix G. IEF Proposal***

IEF Proposal: Fall Term 2010  
Testing the Photocatalytic Oxidation Abilities of Titania-Silica Aerogels  
Fabricated using Rapid Supercritical Extraction  
Mechanical Engineering Senior Project  
Lauren B. Brown  
Advised by Professor Ann M. Anderson

### ***Project Objective***

The objective of this project is to standardize the process for making titania-silica aerogels using the Rapid Supercritical Extraction Method and determine the capability of titania-silica aerogels to perform photocatalytic oxidation for the purpose of eliminating harmful pollutants.

### ***Background***

Heterogeneous photocatalytic oxidation (PCO) is a smart technology for the remediation of organic pollutants since it is economic, simple and easily-implemented. Photocatalytic oxidation is the process of breaking down chemical molecules using light, resulting in harmless products, namely water and carbon dioxide. It has shown promise in the removal of VOCs in process airstreams. VOC are defined as a class of indoor air pollutants found in industrial establishments, manufacturing facilities, commercial workplaces, even homes. Most are simply irritants, but some are suspected to be carcinogens that pose significant long-term health risks. The use of centralized air-handling systems in modern buildings where the air is recycled and recirculated further questions the issue of our exposure to VOCs. PCO has the ability to mineralize simple organic molecules into carbon dioxide and water at ambient conditions using molecular oxygen (Maira et al., 2003).

An aerogel is a porous nanostructure with 90-99% air by volume. It has the lowest known density, index of refraction, thermal, electrical and acoustical conductivities of any known solid. Some applications of a typical silica aerogel include comet dust collectors and electrical insulators for NASA, insulation in jackets, boots and suits for divers, insulating windows, chemical absorber for cleaning up spills, and a platform for sensing chemical species. Aerogels can be difficult to make, however the Rapid Supercritical Extraction (RSCE) method developed by the Aerogel Lab at Union College is able to fabricate aerogels much faster than conventional methods (Gauthier et al., 2004). This method has already been used to make silica (Gauthier et al., 2004; Anderson et al., 2009), alumina (Bono et al., 2010), titania and titania-silica aerogels (Brown, et al. 2010). Titania-silica aerogels are of particular interest due to their properties as an

absorbent and photocatalyst. One application using these properties is adsorption and photocatalytic oxidation to degrade volatile organic compounds (VOCS). One group determined the decomposition of benzene using silica-titania and titania aerogels (Yoda et al. 2000). It was shown that samples containing anatase titania performed better than an amorphous sample. Another group tested the photocatalytic activities of S-doped TiO<sub>2</sub> material under visible light (Ohno et al. 2004). Their results show that S-doped TiO<sub>2</sub> material is able to photocatalytically decompose methylene blue under visible light. These materials may be extremely useful in cleaning up pollutants in air and water, and the faster process that RSCE provides to fabricate titania-silica aerogels would be beneficial.

### *Planned Activities*

For my senior project I will study the ability of titania-silica aerogels fabricated with Union's novel RSCE process to photocatalytically oxidize VOCs from air and determine whether aerogels fabricated with the RSCE method perform better than aerogels made using alternate methods (as reported in the literature). The potential use for this application would be quite widespread and beneficial to the environment and society. To achieve my goal I will perform preliminary experiments to determine whether titania-silica aerogels can decompose chemical molecules. Following this, I will design and build an apparatus that will test how well titania-silica aerogels can break down a harmful VOC.

I will continue to fabricate titania-silica aerogels using a process involving the RSCE method that is much faster than other processes currently in use. The resulting characteristics of titania-silica aerogel samples will be measured including: bulk density, skeletal density, BET surface area and BJH pore distribution.

Next I will test the ability of my titania-silica aerogels to decompose trichloroethylene in a flow-type reactor. This set-up, which I will design and build, will most realistically model a reactor that may be implemented in the vent system of any building to improve the quality of recycled air. Using this setup I will measure how efficiently trichloroethylene is broken down by photocatalytic oxidation using titania-silica aerogels. In the future, a similar apparatus could be designed for implementation in any commercial and industrial building that uses recycled air, to improve the air quality by breaking down harmful VOCs.

### *Budget*

Quantit	Product	Product	Company	Price	Total
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y	Number			each	Price
1	372145-2L	Anhydrous Trichloroethylene (8)	Sigma-Aldrich	\$100.50	\$100.50
1	05-1089	NO4S 4W blacklight with stand (9)	Atlantic Ultraviolet Corp.	\$127.00	\$127.00
				Total:	\$227.50

Funding is being sought to purchase trichloroethylene to use for testing in the apparatus for photocatalytic oxidation. I am also requesting funding for a high quality blacklight to irradiate samples in my testing apparatus. The product I have chosen emits long wave ultraviolet radiation and very little visible light. It also produced energy in the long wave UVA region, peaks at 365 nanometers and has been used for inspection and counterfeit detection purposes. It is important to have a higher quality blacklight so that the exact properties are known. Most other blacklight bulbs I found were for decorative purposes, which would not suit my needs. Any additional chemicals and materials needed to complete the project will be funded by the NSF grant for the Aerogel Lab.

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- (7) Ohno, T., Akiyoshi, M., Umebayashi, T. et al., 2004, *Applied Catalysis A: General*, 265, 115-121.

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- (9) <http://www.ultraviolet.com/pdflib/981341.pdf>

***Appendix H. Green Grant Proposal***

**President's Green Grant Application Form**

**Contact Name:** Lauren B. Brown

**Contact E-mail:** brownl@garnet.union.edu

**Proposed Project Title:** Testing the Photocatalytic Abilities of Titania-Silica Aerogels fabricated using the Rapid Supercritical Extraction Method

**Project Category (please select one):**

- 1) Campus project \_\_\_\_\_
- 2) Research project \_X\_

**Amount of support requested (include a detailed budget in the proposal):**

**\$ 1,941.49**

**Executive summary of proposed project (100 words or fewer):**

The objective of this project is to standardize the process for making titania-silica aerogels using the Rapid Supercritical Extraction Method and determine the capability of titania-silica aerogels to perform photocatalytic oxidation for the purpose of eliminating harmful pollutants. A test apparatus will be designed and built to test the decomposition rate of trichloroethylene using photocatalytic oxidation with titania-silica aerogels. A prototype of a system for placement in any building with recycled air will also be built, in an effort to increase air quality by reducing pollutants.

## *Rationale*

The harmless destruction of toxic pollutants has become increasingly important due to increased reliance on re-circulated air through ventilation systems in commercial and industrial buildings. Technologies that are frequently employed fall into two categories, either conventional phase separation techniques or methods that destroy the contaminants. Chemical oxidation is an example of the latter, which is a more attractive option, since the destruction of chemicals is a more complete solution than phase separation, after which the problem of final disposal still remains. The purpose of chemical oxidation is the transformation of contaminants into harmless products, frequently through mineralization to carbon dioxide, water and inorganics.

Photocatalysis processes use oxygen as an oxidizing agent and a semiconducting metal oxide as a catalyst. The most commonly used catalyst is titanium oxide ( $\text{TiO}_2$ ) in the anatase form. Titania demonstrates high stability, good performance and low cost (Andreozzi, 1999). Pairing a titania catalyst with a material with strong adsorption abilities, such as a silica aerogel, shows promise in the application of photocatalytic oxidation (PCO) to remove volatile organic compounds (VOCs) from process airstreams. VOCs are mostly simple irritants, but some are suspected to be carcinogens that pose significant long-term health risks. The use of centralized air-handling systems in modern buildings where the air is recycled and re-circulated further questions the issue of our exposure to VOCs. PCO has the ability to mineralize simple organic molecules into carbon dioxide and water at ambient conditions using molecular oxygen (Maira et al., 2003).

An aerogel is a porous nanostructure with 90-99% air by volume. It has the lowest known density, index of refraction, thermal, electrical and acoustical conductivities of any known solid. Some applications of a typical silica aerogel include comet dust collectors and electrical insulators for NASA, insulation in jackets, boots and suits for divers, insulating windows, chemical absorber for cleaning up spills, and a platform for sensing chemical species. Aerogels can be difficult to make, however the Rapid Supercritical Extraction (RSCE) method developed by the Aerogel Lab at Union College is able to fabricate aerogels much faster than conventional methods (Gauthier et al., 2004). This method has already been used to make silica (Gauthier et al., 2004; Anderson et al., 2009), alumina (Bono et al., 2010), titania and titania-silica aerogels (Brown, et al. 2010). Titania-silica aerogels are of particular interest in photocatalytic oxidation applications due to their properties as an absorbent and photocatalyst. The faster process that RSCE provides to fabricate titania-silica aerogels would be beneficial to any potential PCO application.

Previous research by one group determined the rate of decomposition of benzene using silica-titania and titania aerogels (Yoda et al. 2000). It was shown that samples containing anatase titania performed better than an amorphous sample. Another group tested the photocatalytic activities of S-doped TiO<sub>2</sub> material under visible light (Ohno et al. 2004). Their results show that S-doped TiO<sub>2</sub> material is able to photocatalytically decompose methylene blue under visible light.

### *Research Plan*

This research is being done to satisfy Mechanical Engineering Senior Project requirements, and will likely involve a third term of research, in addition to the requisite first two terms. I will study the ability of titania-silica aerogels fabricated with Union's novel RSCE process to photocatalytically oxidize VOCs from air and determine whether aerogels fabricated with the RSCE method perform better than aerogels made using alternate methods (as reported in the literature). To achieve this goal I will (1) perform preliminary experiments to determine whether titania-silica aerogels can decompose chemical molecules; (2) design and build an apparatus that will test how well titania-silica aerogels can break down a harmful VOC; and (3) design and build a prototype that can be placed into a ventilation system to utilize photocatalytic oxidation with titania-silica aerogels in any building with recycled air.

I will continue to fabricate titania-silica aerogels using a process involving the RSCE method that is much faster than other processes currently in use. The resulting characteristics of titania-silica aerogel samples will be measured including: bulk density, skeletal density, BET surface area and BJH pore distribution. Previous research has shown this process to be successful in producing aerogels with desirable characteristics in a timely manner.

Next I will test the ability of my titania-silica aerogels to decompose trichloroethylene in a flow-type reactor similar to those used in previous research (Yoda, 2000, Yamazaki-Nishida, 1992). This set-up, which I will design and build, will model a reactor that may be implemented in the vent system of any building to improve the quality of recycled air. Using this setup I will measure how efficiently trichloroethylene is broken down by photocatalytic oxidation using titania-silica aerogels.

Lastly, a prototype apparatus will be designed for implementation in any commercial and industrial building that uses recycled air, to improve the air quality by breaking down harmful VOCs. In designing the prototype I will focus on developing a cost effective system that would require few changes to any ventilation system already in place. Not only would this be an inherently environmentally-friendly process, but it would also save energy that was previously required to continuously draw in outside air.



### *Anticipated Outcomes*

Outcomes to this experiment will include a deeper knowledge of photocatalytic oxidation using titania-silica aerogels. An equally important outcome will be the development of a prototype apparatus to photocatalytically oxidate pollutants in recycled airstreams using titania-silica aerogels. Additionally a PCO test facility for future students studying additional PCO applications will be available.

Since humans spend the majority of their day in buildings with air conditioning systems, it is important that the air quality in these buildings is extremely high. Photocatalytic oxidation using titania-silica aerogels can improve the air quality in an economic and environmentally-friendly manner. The potential benefit of this research to society cannot be overstated.

### *Budget*

Quantity	Item	Part Number	Company	Price Each	Total	Use
4	4W Blacklight Bulb	GE F4T5-BLB		5.80	23.20	test facility
1	Tank of Air	AIUZ300	AirGas	35.00	35.00	test facility
1	Regulator for Air	Y12244A590	AirGas	279.59	279.59	test facility
1	Tank of TCE	303401	Sigma-Aldrich	248.00	248.00	test facility
1	Regulator for TCE	501395	Sigma-Aldrich	167.50	167.50	test facility
1	Reactor Glass Tubing	234102	Corning	197.20	197.20	test/prototype
50kg	Glass Tubing		Jinan GT. Industrial Co.	\$3/kg	150.00	test facility
2	Flow Meters		Flow Network	150.00	300.00	test facility
3	Switching Valves			100.00	300.00	test facility
	Sheet Metal		Quick Ship Metals.com		70.00	prototype
1 bottle	Glass Beads for Reactor	7400-2405	USA Scientific	26.00	26.00	test/prototype
1	Small Fan		Digikey.com		20.00	prototype
	Miscellaneous Supplies				125.00	test/prototype
				Total	1,941.49	

### *Timeline*

**Fall Term:** Background Research – learning more about photocatalytic oxidation applications currently in use

*Second half of the term:* Design test apparatus (currently being done) and price out, order parts

**Winter Term:** Build apparatus with ordered parts; make changes as needed to the system

*Second half of the term:* Test apparatus, determine efficiency of the system and which type of aerogel works best, and alter design for building use

**Spring Term:** Continue to improve design for efficiency, develop system prototype

*Second half of the term:* Build & test system for building use, ideally take next steps to manufacture system for commercial and industrial use

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